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UNIVERSITY OF ALBERTA

THE MINERALOGY AND CHEMISTRY OF GYPSUM BASED BY-PRODUCTS OF PHOSPHATE FERTILIZER PRODUCTION

BY

SHEILA LUTHER

A THESIS SUBMITTED TO THE
FACULTY OF GRADUATE STUDIES AND RESEARCH
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DEGREE OF MASTER OF SCIENCE

IN

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The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research for acceptance, a thesis entitled THE MINERALOGY AND CHEMISTRY OF GYPSUM BASED BY-PRODUCTS OF PHOSPHATE FERTILIZER PRODUCTION submitted by SHEILA M. LUTHER in partial fulfillment of the requirements for the degree of MASTER OF SCIENCE in SOIL CHEMISTRY.

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Dedicated to Berna and Randy

Without their love and support this project could never have been completed.

ABSTRACT

Gypsum based by-products of phosphate fertilizer production, termed phosphogypsum, are stockpiled at several locations in Alberta. Although dominated by gypsum, phosphogypsum contains accessory minerals, trace elements, and radionuclides. This study was conducted to characterize the mineralogy and chemistry of phosphogypsum samples from a plant site in Medicine Hat, Alberta. Parent material from an Orthic Brown Chernozem was also examined. After characterizing the solids, pore water chemistry was studied by equilibrating phosphogypsum, two soil-phosphogypsum combinations, and soil alone with deionized water for up to 90 days; the aqueous phase was then analysed for dissolved constituents. The distribution of ^{226}Ra between solid and solution was also assessed. The solubility controlling solids for major and trace elements were predicted by comparing aqueous ion activities, calculated using GEOCHEM, to theoretical levels estimated from solubility constants.

All of the phosphogypsum samples collected were acidic with pH levels of 4.0 or lower. They were composed primarily of gypsum, however, quartz, phosphate rock and sodium feldspar were also observed. The material was elevated in Ag, Ca, Cd, P, S and Se relative to shale.

For most chemical parameters, the pore water appeared to reach a steady state composition within 28 days. Concentrations of As, Cd, Cr, Cu, Fe, Mn, Na, NO_3^--N, Se, SO_4^{2-}-S, and Zn exceeded drinking water standards (DWS) in some phosphogypsum pore water extracts. Most elemental concentrations decreased to near DWS with soil addition, although some anions did not. No detectable ^{226}Ra was released to the pore water from most samples.

Solubility controlling solids were predicted for Al, Ca, Fe, P, S and Si. Activities of trace ions examined were undersaturated relative to potential solubility controlling solids, however, Cd^{2+}, Cu^{2+}, and Zn^{2+} activities showed a strong inverse relationship with pH. Thus, if leachate from phosphogypsum is neutralised in a calcareous environment, a number of elements would either precipitate as stable solid phases or adsorb onto clays, leaving solution concentrations reduced relative to leachate levels. However, As, NO_3^--N, Se and SO_4^{2-}-S concentrations did not decrease significantly as pH increased; leaching of one or more of these elements into a calcareous environment may elevate normal background levels.

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TABLE OF CONTENTS

CHAPTER I INTRODUCTION 1

CHAPTER II LITERATURE REVIEW 4

- A. INTRODUCTION 4
- B. PHOSPHATE ROCK: ITS ORIGINS, CHEMISTRY AND MINERALOGY 4
  - 1. ORIGINS 4
  - 2. CHEMISTRY AND MINERALOGY 5
  - 3. PATTERNS OF ENRICHMENT 7
- C. PHOSPHATE FERTILIZER PRODUCTION PROCESS 9
  - 1. BENEFICIATION 9
  - 2. PROCESSING 9
- D. SOURCES OF IMPURITIES IN THE PHOSPHOGYPSUM STACK 12
  - 1. PHOSPHATE ROCK 12
  - 2. ATMOSPHERIC DEPOSITION 12
  - 3. SANITARY SEWER 12
  - 4. INDUSTRIAL SEWER 12
  - 5. DRAINAGE DITCHES 13
  - 6. OTHER WASTES 13
- E. PHOSPHOGYPSUM CHARACTERISTICS 13
  - 1. MINERALOGY AND CHEMISTRY 13
  - 2. RADIOACTIVITY 17
  - 3. PORE WATER CHEMISTRY AND THE PREDICTION OF SOLUBILITY CONTROLLING SOLIDS 19
    - i. INTRODUCTION 19
    - ii. CHEMICAL PROPERTIES OF PHOSPHOGYPSUM PORE WATER 20

CHAPTER III MATERIALS AND METHODS 22

A. FIELD SAMPLING 22

B. ROUTINE ANALYSIS 22

C. MINERALOGICAL ANALYSIS 23

1. FRACTIONATION 23

2. CLAY MINERALOGY 25

3. PHOSPHOGYPSUM MINERALOGY 26

D. SCANNING ELECTRON MICROSCOPY 26

E. ELEMENTAL ANALYSIS OF THE SOLID PHASE 26

F. RADIOACTIVITY 27

G. BATCH INCUBATION 28

H. COMPUTER MODELLING 30

CHAPTER IV RESULTS AND DISCUSSION 32

A. CHEMICAL, PHYSICAL, AND MINERALOGICAL PROPERTIES 32

1. CHEMICAL PROPERTIES 32

2. PHYSICAL PROPERTIES 41

3. MINERALOGICAL PROPERTIES 43

i. SOIL CLAY FRACTIONS 43

ii. PHOSPHOGYPSUM 48

B. ELEMENTAL CHEMISTRY OF THE SOLID PHASE 51

1. MAJOR ELEMENTS 51

2. TRACE ELEMENTS 55

3. RARE EARTH ELEMENTS 55

C. RADIOACTIVITY 57

D. PORE WATER CHEMISTRY AND COMPUTER MODELLING 59

1. TIME TRIAL 60

2. EFFECTS OF TIME, TREATMENT AND SOIL ADDITIONS ON PORE WATER CHEMISTRY 73

3. ION DIFFERENCE AND DISTRIBUTION OF SPECIES 76

4. COMPARISON WITH WATER QUALITY GUIDELINES 79

E. SOLUBILITY EQUILIBRIA RELATIONSHIPS 81

1. MAJOR ELEMENTS 83

i. CALCIUM AND SULPHUR 83

ii. PHOSPHORUS 86

iii. ALUMINIUM 88

iv. IRON 90

v. SILICON 93

2. TRACE ELEMENTS 95

i. CADMIUM, COPPER AND ZINC 95

ii. SELENIUM 101

iii. CHROMIUM 103

iv. ARSENIC 105

CHAPTER V SUMMARY AND CONCLUSIONS 107

REFERENCES 112

APPENDIX I 125

APPENDIX II 131

LIST OF TABLES

TABLE 1. Methods used for the analysis of elements in the solid phase 27

TABLE 2. Routine chemical properties of soil and phosphogypsum samples 33

TABLE 3. Chemical properties of saturated paste extracts 35

TABLE 4. Total content (%) of major elements in bulk phosphogysum and soil samples and literature values for terrestrial material 52

TABLE 5. Total content (mg/kg) of some trace elements in phosphogypsum and soil samples and literature values for terrestrial material 53

TABLE 6. Total content (mg/kg) of some rare earth elements (REE) and Y in phosphogypsum and soil samples and literature values for terrestrial material 54

TABLE 7. Levels of ^{226}Ra daughter products in phosphogypsum (peak area/g/24 hours) 58

TABLE 8. Effects of time and treatment on pore water chemistry 75

TABLE 9. Effects of treatment and analytical technique on pore water chemistry 76

TABLE 10. Computer modelled ion difference 77

TABLE 11. Distribution of species (%) in phosphogypsum and soil pore water 78

TABLE 12. Comparison of pore water elemental concentrations (mg/L) with drinking water standards 80

LIST OF FIGURES

FIGURE 1. Sampling locations for seven bulk phosphogypsum samples 23

FIGURE 2. Field profile of phosphogypsum stack showing bedding (depth from surface to approximately 0.5 m) 37

FIGURE 3. Base titration of phosphogypsum sample 5 39

FIGURE 4. Base titration of phosphogypsum sample 6 40

FIGURE 5. Micrographs of the phosphogypsum matrix dominated by well formed gypsum crystals. A, high magnification showing crystal morphology. B, lower magnification showing particle size 42

FIGURE 6. X-ray diffractogram of clay separate from sand sample 44

FIGURE 7. X-ray diffractogram of clay separate from sand sample with $CaCO_3$ removed 45

FIGURE 8. X-ray diffractogram of clay separate from till sample 46

FIGURE 9. X-ray diffractogram of clay separate from till sample with $CaCO_3$ removed 47

FIGURE 10. Micrographs of accessory minerals in phosphogypsum. A, a pitted quartz grain. B, a sodium silicate grain assumed to be a sodium feldspar. C and D, energy dispersive spectra for A and B respectively 49

FIGURE 11. Micrographs of a phosphorus rich area. A, area under high power. B, area under lower power in the bottom left corner within the gypsum matrix. C, energy dispersive spectrum 50

FIGURE 12. Activity of Ca^{2+} over time 61

FIGURE 13. Activity of SO_4^{2-} over time 61

FIGURE 14. Gypsum equilbrium and ion activity product (IAP) over time 62

FIGURE 15. Change in pH over time 62

FIGURE 16. Ionic strength (calculated from electrical conductivity) over time 63

FIGURE 17. Ionic strength (calculated using GEOCHEM) over time 63

FIGURE 18. Activity of Al^{3+} over time 64

FIGURE 19. Concentration of Al over time 64

FIGURE 20. Activity of Fe^{3+} over time 65

FIGURE 21. Activity of Zn^{2+} over time 65

FIGURE 22. Activity of Cd^{2+} over time 66

FIGURE 23. Activity of Cu^{2+} over time 66

FIGURE 24. Activity of $H_2PO_4^-$ over time 67

FIGURE 25. Activity of $H_2SiO_4^{2-}$ over time 67

FIGURE 26. Activity of $HAsO_4^{2-}$ over time 70

FIGURE 27. Activity of $H_2AsO_4^-$ over time 70

FIGURE 28. Activity of $CrOH^{2+}$ over time 71

FIGURE 29. Activity of $Cr(OH)_3^0$ over time 71

FIGURE 30. Activity of SeO_4^{2-} over time 72

FIGURE 31. Activity of $HSeO_3^-$ over time 72

FIGURE 32. Gypsum solubility equilibrium with data from 80 day incubation 84

FIGURE 33. Solubility equilibria for some calcium minerals with data from 80 day incubation 84

FIGURE 34. Solubility equilibria for some phosphate minerals with data from 80 day incubation 87

FIGURE 35. Solubility equilibria for some aluminium minerals with data from 80 day incubation 89

FIGURE 36. Solubility equilibria for some iron minerals with data from 80 day incubation 91

FIGURE 37. Solubility equilibria for some silica minerals with data from 80 day incubation 94

FIGURE 38. Solubility equilibria for some copper minerals with data from 80 day incubation 96

FIGURE 39. Solubility equilibria for some cadmium minerals with data from 80 day incubation 97

FIGURE 40. Solubility equilibria for some zinc minerals with data from 80 day incubation 98

FIGURE 41. Calcium selenate solubility equilibrium with data from 80 day incubation 102

FIGURE 42. Solubility equilibria for some selenite minerals with data from 80 day incubation........102

FIGURE 43. Solubility equilibria for some chromium minerals with data from 80 day incubation........104

FIGURE 44. Solubility equilibria for some arsenic minerals with data from 80 day incubation........104

LIST OF APPENDIX TABLES

TABLE 1. Pore water chemical analyses from the time trial PG1:S0 treatment (mg/L) 131

TABLE 2. Pore water chemical analyses from the time trial PG10:S1 treatment (mg/L) 132

TABLE 3. Pore water chemical analyses from the time trial PG1:S1 treatment (mg/L) 133

TABLE 4. Pore water chemical analyses from the time trial Gypsum treatment (mg/L) 134

TABLE 5. Pore water chemical analyses from PG1:S0(60) (mg/L) 135

TABLE 6. Pore water chemical analyses from PG1:S0(80) (mg/L) 136

TABLE 7. Pore water chemical analyses from PG1:S0(U80) (mg/L) 137

TABLE 8. Pore water chemical analyses from PG10:S1(60) (mg/L) 138

TABLE 9. Pore water chemical analyses from PG10:S1(80) (mg/L) 139

TABLE 10. Pore water chemical analyses from PG1:S1(60) (mg/L) 140

TABLE 11. Pore water chemical analyses from PG1:S1(80) (mg/L) 141

TABLE 12. Pore water chemical analyses from PG0:S1(60) and PG0:S1(80) (mg/L) 142

LIST OF APPENDIX FIGURES

FIGURE 1. Base titration of phosphogypsum sample 1 125

FIGURE 2. Base titration of phosphogypsum sample 2 126

FIGURE 3. Base titration of phosphogypsum sample 3 127

FIGURE 4. Base titration of phosphogypsum sample 4 128

FIGURE 5. Base titration of phosphogypsum sample 7 129

FIGURE 6. Base titration of phosphogypsum sample 8 130

CHAPTER I

INTRODUCTION

Phosphoric acid is an intermediate product required for the production of phosphate fertilizer. It is commonly produced by digesting phosphate rock, which is composed primarily of apatite minerals (calcium phosphates, containing varying amounts of carbonate and fluoride), with sulphuric acid and water to form gypsum, phosphoric acid, and minor quantities of hydrofluoric acid. This process can be illustrated by the simplified reaction (Beall 1966):

$$Ca_{10}(PO_4)_6F_2 + 10\ H_2SO_4 + 20\ H_2O \dashrightarrow 10\ CaSO_4{*}2H_2O + 6\ H_3PO_4 + 2\ HF$$

Thus, a gypsum based by-product is generated which is called phosphogypsum. The term phosphogypsum has been adopted to distinguish this industrial gypsum from the natural mineral. The phospho- prefix is used to indicate that the material originates from phosphate rock rather than to signify the presence of a major phosphorus component.

For every tonne of P_2O_5 produced 4.6 to 5.2 tonnes of by-product gypsum are generated (McBeath 1987). Filtration is used to separate the phosphoric acid from the gypsum and the by-product is transported to settling lagoons, used as a fill for mining cuts or stacked on dry land. The stacking procedure involves pumping the gypsum slurry to stacks that typically reach 30 m in height and cover about 100 ha (Murray and Lewis 1985). Once the solids settle out, pore water is channelled to a cooling pond where it is eventually recycled to the acidulation process.

Annual worldwide production of phosphogypsum was approximately 120 million tonnes in 1988 with estimated production levels in year 2000 at 220 to 290 million tonnes (United Nations 1988). The results of an international survey of the phosphate industry in 1981 showed that 14% of all phosphogypsum was reprocessed, 58% was stored and 28% was dumped (Carmichael 1986). At production capacity, Canadian phosphate fertilizer producers can generate up to 3 million tonnes of phosphogypsum per year based on a 350 day production year (McBeath 1987). In Canada there are approximately 70 million tonnes of the material in storage while in Alberta, 40 million tonnes are stored at refinery sites (SENES 1987) with 1.8 million tonnes being added annually (McBeath 1987).

Phosphogypsum is primarily gypsum (Collings 1980). Impurities which are present include quartz, fluorides, phosphates, organic matter as well as Al and Fe minerals. Phosphogypsum, regardless of the source of the parent phosphate rock, can have elevated levels of various trace elements relative to average elemental levels in the earth's crust. For example, in some phosphogypsum samples from Florida phosphate rock, As has been identified to be a potential problem based on total elemental content in the solid (May and Sweeney 1980). Cadmium and Se were two of the trace elements present at elevated levels in phosphogypsum originating from western rock (Roberts Thorne 1990). Berish (1990) identified As, Cd, Cr, F, Mn, Na, Pb and U^{238} and U^{234} decay products as contaminants of concern in phosphogypsum.

A number of the trace elements present have the potential to be of environmental concern if mobilised from the phosphogypsum and released into the environment. Similarly, many of the major elements present including S, P, and F are not normally considered toxic at concentrations found in natural waters but can have detrimental effects at elevated concentrations, negatively affecting ground water quality (SENES 1987). In addition, levels of N compounds including NO_3^-, which tends to be highly mobile, can be elevated. The N originates primarily from accompanying N fertilizer production processes at some plant sites. Thus, although the phosphate rock is the main source of contaminants in phosphogypsum, other plant inputs are also important.

Phosphate deposits around the world contain appreciable concentrations of radioactive material originating from the decay of U and Th present in the ores (Guimond 1976). Uranium and its decay series are associated with phosphate deposits of marine origin (Roessler 1986). During processing, fractionation occurs with most of the Ra depositing with the phosphogypsum, while most of the U is dissolved through the acidulation of the phosphate rock with sulphuric acid. However, in addition to ^{226}Ra, a number of other radionuclides are of potential concern in phosphogypsum including: ^{238}U, ^{234}U, ^{230}Th, ^{222}Rn, ^{210}Pb, and ^{210}Po (Berish 1990). Groundwater contamination with any of these radionuclides and atmospheric contamination with radon are potential hazards of phosphogypsum stacks.

Although most phosphogypsum is stockpiled, it has a number of possible uses due to its high gypsum content. They include use as a wallboard material, as a component in cement or road building materials and as a soil amendment. Numerous researchers have examined the potential of phosphogypsum as a soil amendment including as a treatment for surface crusting and reduced infiltration in sodic soils (Agassi *et al.* 1986; Gal *et al.* 1984; Keren and Shainberg 1981; Mishra 1980; and Oster 1980), for acidic subsoils (Alva *et al.* 1990, 1991; Alva and Sumner 1990;

O'Brien and Sumner 1988; and Sumner *et al.* 1986a, b), and for soils deficient in Ca and S (Baird and Kamprath 1980). It has been recommended over coarse grade mined gypsum as a soil amendment because of its higher solubility due to a smaller particle size (Mishra 1980).

Utilisation of phosphogypsum has been restricted, particularly in North America, due to environmental and economic limitations as it must compete with mined natural gypsum for various applications (Berish 1990; Collings 1980). Although the presence of contaminants restricts phosphogypsum uses, little information is available on their form and leaching behaviour. Most work has focused on reprocessing and utilisation, field monitoring to assess contaminant mobility, and radon emissions. Although a number of studies have examined the elemental content of phosphogypsum, few have examined the leaching characteristics of the material. Studies have yet to be conducted to establish the equilibrium pore water concentrations of major and trace elements in phosphogypsum, making use of this information to predict the solubility controlling solids present. Solubility controlling solids if identified can be used in estimating maximum expected limits of a elemental concentrations in the pore water (Mattigod *et al.* 1990) and are thus important for determining the safety of phosphogypsum disposal and utilisation. This study was initiated with the following objectives:

1. To characterize the mineralogy and chemistry of representative samples of the by-products of phosphate fertilizer production in Medicine Hat, Alberta,

2. To document the total trace element content and distribution of radioactivity (Ra^{226}) for these samples,

3. To conduct chemical incubation studies and pore water extractions of phosphogypsum including "aged" and acidic material as well as mixes of soil and phosphogypsum in order to establish solution chemistry parameters, and

4. To perform computer analyses of the pore water chemistry of the phosphogypsum and phosphogypsum-soil mixes using a current thermodynamic geochemical model, in order to evaluate theoretical predictions versus empirical measurements.

CHAPTER II

LITERATURE REVIEW

A. Introduction

The mineralogy and chemistry of phosphogypsum are a function of the parent phosphate rock along with secondary sources of contaminants which are released into the phosphogypsum stack through the industrial process. Although this project was essentially a case study focusing on by-product samples from one stack located in the city of Medicine Hat in southeastern Alberta, much of the fundamental chemistry and mineralogy examined is relevant to any phosphogypsum stack.

In this review information is provided on the factors governing the mineralogy and chemistry of phosphogypsum with an emphasis on the source rock and processes used at the Medicine Hat plant. The mineralogical and chemical nature of phosphogypsum can be related to studies of other waste materials and contaminated soils. Thus a theoretical discussion of the expected solubility controlling solids for major and trace elements is provided which is based on studies of related industrial by-products, geological materials, trace element contaminated soils and phosphogypsum itself.

B. Phosphate Rock: Its Origins, Chemistry and Mineralogy

1. Origins

Beneficiated ore utilised at the Medicine Hat plant came almost exclusively from the western United States, specifically from sources in southeastern Idaho, although a small amount originated from Florida. Rich deposits of phosphorite, a sedimentary rock composed entirely of apatite, covering an area of 350,000 km^2 within the states of Idaho, Wyoming, Montana, Utah and northeastern Nevada, make up the Phosphoria Formation. The beds are of Permian age and are composed of phosphorite, shale, and carbonate rock, intermixed with organic matter and chert (Gulbrandsen 1974). There are two phosphatic shale members: the Meade Park and the Retort. The rich deposits of southeastern Idaho are part of the Meade Park Member which ranges in thickness from about 34 to 69 metres at this location.

Phosphorite is made up of microcrystalline carbonate fluorapatite in the form of lamillae, pellets, oolites, nodules, skeletal, shell, and bone fragments (Bates and

Jackson 1980). The sedimentation of phosphorite and organic matter forming the Phosphoria Formation was likely due to high planktonic biotal productivity of the ocean surface where nutrient-rich deeper ocean water welled up (Sheldon 1989). Settling of dead organic debris to the sea bottom of the shallow basin and shelf transferred phosphorus-containing organic matter to sediments where early diagenetic, bacterial decay liberated phosphorus, making it available for the formation of phosphorite.

2. Chemistry and Mineralogy

Carbonate fluorapatite (francolite) is the phosphate mineral of all marine sedimentary phosphate deposits (MacDonald 1987). Within the structure of fluorapatite:

$Ca_{10}(PO_4)_6F_2$

CO_3 commonly is substituted for PO_4 at levels of approximately 2 to 3% carbonate (Altschuler *et al.* 1958). Other substitutions that can occur include SO_4 for PO_4, and Na and Mg for Ca. Strontium, Na, U, Th and the rare earth elements and Y can also substitute for Ca (Gulbrandsen 1967; Cathcart 1980). The average Phosphoria phosphorite has a mineral composition of approximately 80% apatite, 10% quartz, 5% muscovite-illite, 2% organic matter, 1% dolomite-calcite, 1% iron oxide and 1% other components (Gulbrandsen 1966). Quartz, muscovite-illite, iron oxide and organic acid are essentially ubiquitous components of phosphorites in addition to apatite (Gulbrandsen 1967). The most common Fe-Al oxides and hydroxides identified in sedimentary phosphate rock are goethite, limonite, bauxite minerals and barbosalite (McClellan and Gremillion 1980). Buddingtonite $(((NH_4)_{0.82}\ K_{0.15}\ Na_{0.03})\ AlSi_3O_8{*}0.44H_2O)$, an unusual feldspar containing ammonium, has been found to occur in large quantities in certain beds of the Phosphoria Formation (Gulbrandsen 1974). It is distributed widely in the rocks of the Meade Park Member occurring in amounts as high as 50%. Other accessory minerals which occur in phosphate rock include titanium minerals such as rutile, ilmenite, anatase, and perovskite (McClellan and Gremillion 1980). Iron sulfides such as pyrite and marcasite are also minor accessories and fluorite is commonly found particularly in rocks of the Phosphoria Formation. Tourmaline, montmorillonite, kaolinite and sphene have also been identified in some phosphorites (Gulbrandsen 1967).

An apatite pellet composite from the Phosphoria Formation was reported to be made up of 37% P_2O_5 and 4% F (Sheldon 1989). There is generally an excess of F, based on the structure of fluorapatite, which is assumed to be in CO_3F groups which replace PO_4 (McClellan and Lehr 1969). Due to the intimate mixture of silt, clay, organic matter and minor carbonate in pellets, it is impossible to get pure apatite for analysis. Within black phosphorite layers of the Meade Park Member, average levels of P_2O_5 were 29.8% (Gulbrandsen 1966).

Silicon, Al, Fe, Mg, Na, and K levels in 40 samples of Meade Park phosphorite from Gulbrandsen (1966) were less than average levels in shale or crustal materials (Krauskopf 1979), while Ca, P, and F were elevated relative to the same standards. The material had an average organic matter content of 2.3% with samples ranging from 0.5 to 8.0%. Oil content was as high as 2.1%. The organic matter of the dark phosphatic shale members of the Phosphoria Formation likely served as the source of petroleum in the upper Carboniferous-Permian oil province of central Wyoming (Sheldon 1989). The organic content can be detrimental during processing, except in those plants which use it as a supplementary source of fuel for calcining to remove organic matter and F.

Phosphorites as a group as well as Phosphoria phosphorite are enriched relative to shales in a large number of trace elements. Average elemental abundances in phosphorites have been compared to those of shale (Krauskopf 1979) since both are of marine origin; moreover, shale is the most common surface rock and clearly is a superior basis over total crustal abundances for evaluating environmental stress due to phosphorite occurrence or utilisation (Altschuler 1980). For the phosphorites as a whole, the trace elements enriched, listed in order of degree of enrichment, are Cd(60x), U(30x), Ag(20x), Se(8x), Y(7x), Yb(4x), Mo(4x), La and Nd (each 3x), and As, Sr, Pb, and Zn (each 2x). All rare earth elements (elements from atomic number 57 to 71) except Ce show enrichment. The elements depleted in phosphorite are Li(12x), Ti(7x), B, Ga, and Hg (each 6x), Co and Zr (each 3x), and Sn and Th (each 2x). The elements of normal abundance are B, Ba, Be, Ce, Cr, Cu, Mn, Ni, and Sc. Similar trends are apparent in the Phosphoria phosphorite (Gulbrandsen 1966), the notable exceptions, where data are available, are Ag(60x), Mo(50x), Se(20x), Nd(10x), and As(4x) which are even more enriched and Zr(6x) which is even more depleted; Cr(10x), and Cu and V (each 2x) show some enrichment while Mn(30x), and Ba(6x) show depletion. Although Pb is enriched in average world phosphorite it is depleted by >2x in Phosphoria phosphorite.

Florida phosphate ores contain between 0.20 and 9.9 Bq g^{-1} U^{238}, 0.015 to 0.15 Bq g^{-1} Th^{232} and equivalent activities of their radioactive daughters (SENES 1987). The concentration of the Th^{232} chain is so small that it is often ignored for the purposes of dose assessment (Metzger *et al.* 1980). For comparison, surface soil typically contains U^{238}, Ra^{226}, and Th^{232} concentrations of approximately 0.01 to 0.07 Bq g^{-1} (Myrick *et al.* 1983).

3. Patterns of Enrichment

Elements present in phosphate rock may occur as mineral phases, substituted into the crystal structure of accessory mineral phases, substituted into the dominant apatite structure or associated with the organic fraction. Cadmium, Pb, Sr, U, Y and rare earth elements (REE), and Zn are known or may be presumed on crystallo-chemical grounds to substitute for Ca in apatite (Altschuler 1980). They tend to be more concentrated in purified marine apatite than in less pure phosphorites. Charge balances are obtained through further substitutions: Na^+ for Ca^{2+} and $SiO_4{}^{4-}$ for $PO_4{}^{3-}$. The levels of Na^+ and $SiO_4{}^{4-}$ in marine sedimentary apatite are more than adequate to supply the required charge balance for species such as U^{4+} and REE^{3+}. Enrichment of Bi may be due to substitution for Ca, and it is possible that K, Mg, and Mn also substitute for Ca (McConnell 1938). Arsenic, V, and C may substitute for P within in the apatite structure.

Zinc and Cd are both enriched in phosphorites. As a general rule in most large classes of rock, the abundance of Zn exceeds that of Cd by a factor of several hundred (Altschuler 1980). In phosphorites, Cd is differentially enriched over Zn with the ratio of Zn/Cd being near 10. This suggests that the closeness of the ionic radii of Cd and Ca which are almost identical versus the difference between Zn and Ca by a factor of 20 has imparted a crystallo-chemical favourability to Cd. Thus, where Cd is high without comparable increases in Zn, Cd is being preferentially fixed in an apatite structure. Zn and/or Cd may also be associated with sphalerite and Mn minerals in phosphorites.

In felsic and intermediate igneous rocks the ratio of Th to U is generally 3 to 4 (Altschuler 1980). In contrast, the Th/U ratio in sea water is reported to be approximately 0.006 (Baranov and Kristianova 1959). Uranium may move into the solution phase more readily due to a tendency to be oxidized to hexavalent $(UO_2)^{2+}$ cation complex, which readily complexes with carbonate in solution. Tetravalent Th^{4+} in contrast tends to coprecipitate with oxidate minerals like iron and manganese oxides, and with clays. Thus average detrital shales and sandstones display Th/U ratios like those of igneous rocks ranging from 2.5 to 4.0 (Vinogradov and Ronov 1956), while the Th/U ratios in marine phosphorites are of the order of 0.05 to 0.07 (Altschuler 1980). The ratio in phosphorites may be attributed to the general paucity of

Th in seawater and to the adaptability of the apatite structure to coupled and compensatory replacements, such as SiO_4^{4-} for PO_4^{3-}, which is the same feature which permits the enrichment of rare earth elements (REE) in marine and igneous apatite.

Yttrium, which behaves similarly to the REE, is considered to be so highly enriched in phosphorites relative to shales due to its corresponding abundance in seawater which is a reflection of the precipitation or fixation of the element from a seawater source (Altschuler 1980). Cerium is unique in the REE in that it shows no enrichment which may be explained by its corresponding deficiency in seawater. However, in general the relative abundance of various elements in seawater compared to shale seems to have little bearing on the abundance in phosphorites according to Altschuler (1980) which is contrary to conclusions of earlier studies (Tooms *et al.* 1969).

Enriched levels of Ag, Se, Mo and As as well as the presence of Ni, V, Zn and Cr in phosphorites have been attributed to organic complexing or adsorption (Krauskopf 1955). Copper, Cd, and Sb have also been included among this group (Gulbrandsen 1966). This is explained by the well-established enrichment of these elements in bituminous shales and in the finding in the Phosphoria Formation that these elements are most concentrated as a group and individually in samples which are richer in organic matter. It is also possible that the observed correlation with organic matter content is attributable to the dependence of H_2S generation and the consequent production of metallic sulfides on a reducing regime induced by an excess of organic accumulation over available oxygen. In phosphorites, As and Mo have been found in pyrite and secondary hydrous iron oxides (Blisskovskiy *et al.* 1968, Blisskovskiy 1969). High levels of Zn and Cd in the Phosphoria Formation have been attributed to sphalerite (Desborough 1977 as cited by Altschuler 1980) and both V and Cr may be concentrated in iron oxides and clays at high concentrations (Blisskovskiy 1969).

Those elements depleted in phosphorites fall into two groups. Those in the first group occur in relatively stable insoluble minerals which are more abundant in highly detritus rich shales than in largely chemogenic phosphates (Altschuler 1980). This group includes Ga in clays, Zr in zircon, and Ti in ilmenite and rutile. Members of the other group possess ionic radii (Li and Co) or anionic configurations (BO_3) which are not accommodated into the apatite structure. Barium, Ni, Se, and V also fit into this group. Any enrichment in these elements is likely due to other processes.

C. Phosphate Fertilizer Production Process

1. Beneficiation

Mined phosphate rock was beneficiated in Idaho prior to being transported to Medicine Hat, Alberta. This process is used to bring the P content of the material to greater than 30 percent P_2O_5 (Axelrod *et al.* 1980), which is optimum for commercial phosphates. Beneficiation requires two steps, liberation and separation (McClellan and Gremillion 1980). Liberation usually involves size reduction or particle detachment permitting separation of the desired minerals. In some high grade phosphate rocks, size reduction followed by screening to remove over and under size materials is all that is necessary prior to processing. In others, a further concentration step involving washing, flotation, calcination, magnetic separation or electrostatic separation is required. Phosphate rock is often concentrated by a combination of washing, flotation, and calcination. The beneficiation process implemented on western rock prior to shipment to Medicine Hat involved grinding, washing out the clays, and calcination in large fluidized beds (Gallagher 1991).

Organic compounds, derived from fossilized plants and animals or from beneficiating reagents used in processing the rock, can cause foaming during the acidulation process along with discolouration of the products which may decrease their market value (McClellan and Gremillion 1980). For these reasons calcination was required as part of the beneficiation of western phosphate rock involving the crushing of the rock and calcination at 910^{o}C to reduce the organic content to approximately one percent (Norris 1969). Calcium carbonate also contributes to foaming and it can be minimised by calcining which transforms carbonates to oxides and is followed by slaking to separate the hydrated oxides from the phosphate (Robinson 1980).

2. Processing

The plant in Medicine Hat began operations in 1956 and was in operation for 26 years. Presently the plant site is being decommissioned. Approximately 12 million tonnes of phosphogypsum tailings are stored in a glacial channel adjacent to the plant which had no prior base preparation. The stack reaches a depth of up to 5 metres (Roberts Thorne 1990) and covers 180 hectares which is the largest area of any stack of its type in Canada (SENES 1987). After start up, a system of dykes was constructed and the gypsum pond was divided into seven discrete cells. At the northern end of the original stack, a clear well was used to collect clarified water from the pond cells and return it to the phosphate plant to be recycled. The stack is located in the northwestern corner of the city of Medicine Hat with its nearest edge 1150 metres north of the closest residential development and 900 metres southwest of the nearest shore of the South Saskatchewan river (Roberts Thorne 1990). Presently, there are two active phosphate fertilizer plants in Alberta which have a total production capacity level of approximately 5.3 thousand tonnes of phosphogypsum per day (McBeath 1987).

There were six primary process streams used to produce fertilizer at the Medicine Hat plant, with the final products being ammonium phosphate and ammonium nitrate. The intermediate products of the first four plants, ammonia, sulphuric acid, nitric acid and phosphoric acid, were used to produce the final products. Wastes from the various production processes entered the phosphogypsum stack and thus each process is discussed briefly here, much of the information originating from a study by Roberts Thorne (1990).

The production of ammonia involved the reaction of nitrogen from air with hydrogen supplied by natural gas to produce liquid anhydrous ammonia. At the sulphuric acid plant elemental sulphur was melted and ignited forming SO_2. A vanadium pentoxide catalyst was used to convert SO_2 to SO_3. In an adsorption tower containing ceramic packing, SO_3 was reacted to form H_2SO_4 (93%) after reverse-flow contact with recycled sulphuric acid. In the nitric acid plant the liquid anhydrous ammonia from the ammonia plant was vapourized and mixed with compressed air and ignited over a platinum rhodium gauze catalyst to produce nitrous oxides. In a cooler condenser the nitrous oxides were converted to nitrogen dioxide. Nitric acid was produced by running this gas through a bubble cap absorption column with a counter current of water.

Wet process phosphoric acid production involves digesting a slurry of phosphate rock with sulphuric acid; the phosphoric acid is then separated from the solid products of the reaction by filtration. The principal reaction is as follows (Robinson 1980):

$$Ca_{10}(PO_4)_6F_2 + 10\ H_2SO_4 + 10x\ H_2O \dashrightarrow 10CaSO_4xH_2O + 6\ H_3PO_4 + HF$$

Where x = 0, 0.5 to 0.7, or 2.0

The two most common methods are the dihydrate ($CaSO_4*2H_2O$) and hemihydrate ($CaSO_4*1/2H_2O$) processes, the name being a function of the mode of calcium sulfate precipitation. The dihydrate process, which was used in Medicine Hat, is well-established as the main wet process route. The hemihydrate process uses higher temperatures and acid concentrations in the reaction tanks which favour the initial formation of hemihydrate (May and Sweeney 1984). Subsequently hemihydrate is mixed with gypsum suspensions and it crystallizes as dihydrate. The liquid phase contains 28 to 30% P_2O_5 with the dihydrate process and 40 to 50% P_2O_5 with the hemihydrate process (Hurst and Arnold 1980). The specific process in use has an effect on the partitioning of trace constituents between the solid and liquid phases.

The first step in phosphoric acid production in Medicine Hat was the fine grinding of phosphate rock in a ball mill, after which it was wetted in agitated tank. The finely ground phosphate rock was digested with (93%) sulphuric acid in a reaction tank. In general in the dihydrate process, the digester reaction time ranges from 3 to 8 hours to permit complete crystallization of calcium sulfate, with the temperature being maintained at $80^{o}C$ (McBeath 1987). The reaction is exothermic and thus requires some cooling. The concentration of acid is critical in the process as in the presence of sulphate ions a solid layer of calcium sulphate may form around the rock grains, inhibiting diffusion and thus reducing the reaction rate (Robinson 1980).

The phosphoric acid and phosphogypsum were separated by filtration with the phosphogypsum being sluiced to the stack, and the phosphoric acid being concentrated prior to the next stage in the process. Hydrogen fluoride is a third product of the acidulation process. It reacts with silicon in the rock to produce silicon tetrafluoride (SiF_4), which hydrolyzes to form fluorosilicic acid (H_2SiF_6) (McBeath 1987). At high temperatures, the acid decomposes releasing gaseous silicon tetrafluoride and hydrogen fluoride. The evolved gaseous fluoride is usually recovered as fluorosilicic acid by absorption in water using a scrubber with recycling facilities. At the Medicine Hat plant the waste water from scrubbing and digesting was cycled though the phosphogypsum stack until the solids settled out; the process water was then recycled through the acidulation process.

In order to produce ammonium phosphate, ammonia, phosphoric acid and varying amounts of sulphuric acid were mixed in a reaction vessel and agitated to produce an ammonium phosphate slurry. In a granulator the slurry was converted to ammonium phosphate granules. Once these were cooled and dried, the final product was ready for packaging. Ammonium nitrate fertilizer production involved the reaction of heated nitric acid with ammonia in a packed column; the product was solidified, cooled and coated.

D. Sources of Impurities in the Phosphogypsum Stack

Five main sources of impurities at the Medicine Hat plant have been identified (Gallagher 1990 as cited by Roberts Thorne 1990).

1. Phosphate Rock

The major component making up the tailings pond is gypsum produced through the acidulation of phosphate rock. Thus the main source of impurities to the stack is the phosphate rock itself. Trace elements present in phosphate rock which are not passed on to the fertilizer product are carried to the stack in the phosphogypsum slurry.

2. Atmospheric Deposition

McBeath (1987) listed the major emission problems associated with the production of phosphate fertilizers as fluorides, particulates, ammonia, sulphur dioxide, and acid mists. At the Medicine Hat plant a scrubber was used to trap gaseous fluorides vented from the digestion and evaporation in the phosphoric acid plant, however some fluorides escaped to the atmosphere (Gallagher 1991). Dust components included ammonium phosphate and ammonium nitrate particulates, aluminium oxide, portland cement, emery, kaolin, silica, mineral wool fiber and phosphate rock.

3. Sanitary Sewer

Human and laboratory wastes were carried to the phosphogypsum stack through the sanitary sewer until 1981 when the plant was tied into the Medicine Hat municipal sewer system. Over 340 chemicals were in use in the laboratory and of these a number had a relatively high frequency of use including barium and cadmium chloride, lead dioxide, mercury compounds, elemental mercury and silver nitrate.

4. Industrial Sewer

Wastes from all process streams except the ammonium phosphate plant were carried to the phosphogypsum stack via the sanitary sewer. The ammonium phosphate plant wastes were routed to the tailings flume. Wastes entering the sewer included cooling tower and boiler feed water blowdowns, which contained several water treatment chemicals. In addition, steam condensate, softener backwashing, instrument blowdown, cooling water from pumps and bearings and settling basin overflow were drained though the industrial sewer. Plant spills and leaks were also disposed of in this way.

5. Drainage Ditches

A surface drainage ditch system directed most plant site run-off to the tailings pond. Potential contaminants included nitrates, phosphates, oil and grease, phosphate ore, and spilled materials (Norlander and Revel 1989 as cited by Roberts Thorne 1990).

6. Other Wastes

The majority of solid waste produced at the Medicine Hat plant other than the phosphogypsum tailings were not disposed of in the stack but rather were landfilled both on- and off-site, or incinerated at a designated on-site landfill. In recent years, the recycling of chemical compounds was implemented.

E. Phosphogypsum Characteristics

1. Mineralogy and Chemistry

Phosphogyspsum is an acidic, finely divided material which contains over 90 percent gypsum (Collings 1980). Depending on impurities in the phosphate rock and the conditions maintained during the acidulation process, gypsum crystals may be needle-like to tabular. Some describe the crystal morphology as rhombohedron shaped (Robinson 1980) or as large crystals (0.01 to 0.03 mm) of isometric to prismatic shapes (Tsarevskii 1984). No marked signs of aggregation or mutual organization of crystals has been observed.

The acidic nature of phosphogypsum is attributed to residual phosphoric acid produced during the acidulation process (Moisset 1980). With aging the acidic nature of phosphogypsum is modified presumably by the leaching of acid. In core samples through inactive phosphogypsum stacks, which were examined by May and Sweeney (1980), the pH near the surface was somewhat elevated over the pH deeper in the stack. In a study that compared leachate samples from an active and an inactive stack, the active stack leachate had a pH of 3 while the pH of the leachate from the stack inactive for 10-15 years was 6 (SENES 1987). This variation in pH has a major effect on the solution chemistry.

Common impurities in phosphogypsum include unreacted or partially reacted phosphate rock, organic material, calcium fluoride and quartz sand (Collings 1980). May and Sweeney (1980) observed that the only mineral other than gypsum which was detectable in the by-product, using x-ray diffraction with a limit of detection of 5% of the sample, was α-quartz. The phosphate rock which remains with the gypsum is present due to the coating of phosphate rock with gypsum crystals during the acidulation process therefore blocking the breakdown of a portion of the phosphate rock present (Robinson 1980). Normally phosphorus losses arising from the coating of rock grains by calcium sulphate are low in a well-operated plant. The extent to which the coating occurs is dependent on the choice of sulphate concentration in the reaction system where the rock is added. Phosphorus can also occur within the gypsum structure through the substitution of HPO_4^{2-} for SO_4^{2-} (United Nations 1988).

Typical dihydrate phosphogypsum analysis includes: 32.5% CaO, 44.0% SO_3, 0.65% P_2O_5, 1.20% F, 0.50% SiO_2, 0.10% Fe_2O_3, 0.10% MgO, and approximately 19.0% crystalline H_2O (Kouloheris 1980). Relative to shale (Krauskopf 1979) the material is typically enriched in Ca, F, P, and S and depleted in Al, Fe, K, Mg, Na, Si, and Ti (Kouloheris 1980; May and Sweeney 1984).

Some of the major elements which are enriched have the potential to be of an environmental health concern if excessive levels occur in ground or surface waters. At F^- concentrations in drinking water in the range of 1-2 mg L^{-1} dental fluorosis can occur and crippling fluorosis may develop at consumption levels of 10-40 mg day^{-1} of F^- (De Zuane 1990). Fluoride in doses of 250-450 mg gives severe symptoms causing death when it the dose reaches 4 g. Sulphate may have a cathartic effect at greater than 500 mg/L (Federal-Provincial Subcommittee on Drinking Water 1989) and based on taste, the United States drinking water standards set the limit at 250 mg/L (De Zuane 1990). The orthophosphate ion in surface waters contributes to algal blooms which lower the dissolved oxygen concentration. Nitrogen levels can also be elevated in phophogypsum and NO_3^-, which is highly mobile, is regulated in drinking water because when converted to nitrite it can oxidise blood hemaglobin making it ineffective in oxygen transport. It is also associated with nuisance growths of aquatic organisms such as algae (Task Force on Water Quality Guidelines 1987).

The form of major and trace elements in the solid can be attributed to a number of processes including precipitation in an essentially pure mineral phase, coprecipitation within a solid solution and adsorption on the surface of organic or mineral components. For many of the major elements discussed above, the first two processes are expected to dominate the activity of the ion in solution. Fluorine levels in the solid can range up to 4% with fluorite along with fluorapatite being potential solubility controlling solids (Murray and Lewis 1985; Jenne *et al.* 1980). Phosphorus likely remains in an apatite or fluorapatite mineral, however gypsum may also contain some lattice P_2O_5 through the replacement of SO_4^{2-} by HPO_4^{2-} (United Nations 1988). Solution Si levels are expected to be controlled by amorphous SiO_2 (Rai *et al.* 1987a), quartz or some SiO_2 mineral of intermediate solubility (Lindsay 1979). The Ca, S and crystalline H_2O likely occur primarily in the form of gypsum.

Other common metals present at lower levels may occur in sulphate, or phosphate minerals, particularly in acidic phosphogypsum under aerobic conditions such as in the case of Al and Fe. Alumino sulphate minerals such as alunite and basaluminite have been identified as forming in some soils and sediments (Adams and Rawajfih 1977; Nordstrom 1982; Singh and Brydon 1969) since they are more stable than gibbsite at relatively low pH values (<4) and high sulphate activities ($>10^{-3}$) (Lindsay 1979; Sposito 1989). In acidic pH ranges and in the presence of greater than 10^{-3} molar K^+ and SO_4^{2-} activity, jarosite and iron sulphate may control Fe^{3+} activity (Rai *et al.* 1987). Other potential solubility controlling solids for iron include iron hydroxides, oxides and oxyhydroxides (Lindsay 1979).

The trace elements present in the by-product were measured in some samples from the phosphogypsum stack at Medicine Hat by Roberts Thorne (1990). In comparison with shale (Krauskopf 1979) the phosphogypsum samples were enriched in Ag(40x), Cd(30x), Se(20x), and Y and La (each 2x). Most elements showed a depletion of up to 10x. Those showing even greater depletion included Mn(300x), Th(20x), and B and Sc (each 15x). Those nearly the same as shale were Dy, Eu, Nd, Ni, Sr, Tb, U, and Yb. All of the rare earth elements (REE) measured were either equivalent to or enriched relative to shale except Ce which was depleted, reflecting their distributions in phosphate rock. Of the REE and Y, Y and La showed the greatest enrichment.

The elevated levels of some of the trace elements also have the potential to be of environmental concern. Silver as Ag^+ is one of the most toxic heavy metals to a range of life forms including microorganisms, and fish. (Jones 1939; Shaw 1954; Liang and Tabatabai 1977). Cadmium can be a hazard to human health mainly by its chronic accumulation in the kidneys where it can cause dysfunction if the concentration in the kidney cortex exceeds 200 mg kg^{-1} fresh weight (Fasset 1980). Chronic toxicity from daily average consumption of 4.8 mg Se has been reported in China (De Zuane 1990). In animals it has caused acute chronic toxicity at high levels resulting in congenital muscle disease. However, minimum nutritional requirements for Se are about 100-200 ug day^{-1} for an adult and 0.1 mg kg^{-1} in food for animals and its deficiency can result in white muscle disease in animals (Allaway 1969). Arsenic, Cr and Pb have also been identified as of potential environmental concern in some phosphogypsum (Berish 1990). They can be highly toxic and their levels are regulated in drinking water (De Zuane 1990).

As with the major metals, many of the trace metals present may occur in the form of sulphate, phosphate or carbonate minerals as the phosphogypsum ages. Trace ligands may form minerals with Ca or other common metals. In the case of silver, Ag^{+} is easily reduced and thus is not readily accessible to living organisms in the natural environment. Silver likely forms halide minerals in both oxidised and reduced conditions (Lindsay and Sadiq 1978). Organically bound Ag may also be an important form of attenuation (Boyle 1967). For Se, selenite (SeO_3^{2-}) is the most redox stable form over selenate (SeO_4^{2-}) (Neal 1990). Its solubility may be controlled by $MnSeO_3$ (Elrashidi *et al.* 1987) and $CaSeO_3{*}2H_2O$ (Neal *et al.* 1987) in acid soils. Lead selenite appears to be most stable in alkaline soils (Elrashidi *et al.* 1987). Under reduced conditions Cu_2Se, PbSe, and SnSe prevent the precipitation of elemental selenium. In some soils ferric oxide selenites could be important (Geering *et al.* 1968) and a soil complex involving gypsum and selenite may also attenuate soluble SeO_3^{2-} (Neal 1990). Most selenate and selenite solids are too soluble to act as solubility contols for Se under oxidising conditions expected for most waste-leaching environments (Rai *et al.* 1987a). Thus, adsorption reactions may be the major controls on Se concentrations under such conditions.

Along with selenium-gypsum precipitation, a number of researchers have examined the formation of cation substituted calcium sulphate based solid solutions such as with Cd^{2+} (Van Der Sluis *et al.* 1986), Sr^{2+}, Mg^{2+}, Na^{+}, K^{+}, or with the anion, Cl^{-} (Kushnir 1980). Two possible mechanisms have been identified, that is direct isomorphous substitution of Cd^{2+} for Ca^{2+} in the calcium sulphate lattice (Witkamp and Van Rosmalen 1986) or for ions less similar in ionic radius to Ca^{2+} such as Sr^{+2} of Mg^{+2}, they may occupy interstitial lattice positions in the gypsum, most likely among the water molecules (Kushnir 1980). Within the gypsum structure there are large openings among the water molecules with radii as large as 0.1 nm which may be filled with Mg^{+2}, Sr^{+2}, Na^{+} or K^{+} with only slight to no distortion. The rare earth elements and Y which are present in phosphogypsum may also occur as a solid solution with calcium sulphate. Most are close to Ca^{2+} in ionic radius and so may substitute for Ca^{2+} within the gypsum structure, as in the case of Cd^{2+}.

2. Radioactivity

Phosphate rock contains minor quantities of radioactive material made up mainly of the disintegration products of the ^{238}U series along with minor quantities (about 5%) from the ^{232}Th series (Lardinoye *et al.* 1982). Most phosphate ores contain approximately 1.5 Bq g^{-1} of ^{238}U, 0.6 Bq g^{-1} of ^{232}Th and 1.5 Bq g^{-1} of ^{226}Ra. Within phosphate rock the members of the U and Th decay series are in approximate radioactive equilibrium but upon acidulation in wet process phosphoric acid production, there is a re-distribution of radioactivity (Roessler 1986). Since a number of the chemical properties of Ra are equivalent to those of Ca, most of the Ra is partitioned into the phosphogypsum (Lardinoye *et al.* 1982). The U remains in liquid phase in the form of uranyl complexes primarily with phosphate (Moisset 1980). Thus in phosphoric acid production, more than 90% of the Ra ends up in the gypsum while over 90% of the U is transferred to the phosphoric acid. The ^{232}Th and ^{210}Pb move with the U to the liquid phase while over 90% of the ^{210}Po moves to the phosphogypsum (Hurst and Arnold 1980). Once the phosphogypsum is filtered off, the equilibrium between ^{226}Ra and its disintegration products is restored after about two weeks (Lardinoye *et al.* 1982).

In a Florida based study, the radionuclide concentrations of phosphogypsum exceeded those in background soils by 10 times for ^{234}U and by 60 times for ^{226}Ra (Berish 1990). Radium levels in samples from the Medicine Hat phosphogypsum stack were 0.5 Bq g^{-1} on average (Roberts Thorne 1990). Average levels of Ra in United States soils are in the order of 0.018 to 0.037 Bq g^{-1} (Roessler 1990). Therefore the Medicine Hat samples showed a Ra enrichment ranging anywhere from 14 to 27 times over a typical soil.

Radioactive decay in the atmosphere leads to the production of airborne short-lived radon decay products. When they occur in sufficiently high concentrations in underground mines, airborne radon decay products have been associated with lung cancer and it is presumed that exposure to lower concentrations presents a proportional risk (Roessler 1990). The radionuclides of an environmental concern in phosphogypsum include ^{238}U, ^{234}U, ^{230}Th, ^{226}Ra, ^{222}Rn, ^{210}Pb, and ^{210}Po (Berish 1990). Radium-226 is a long-lived alpha emitter that follows chemical and biological pathways similar to Ca (Roessler 1986). Polonium-210 is an alpha emitter and hence a potential hazard inside the body. In the absence of ^{210}Pb it would not be persistent since its half life is only 138 days. The beta-emitting ^{210}Pb is less of a hazard in itself but it is mobile biologically and serves as a persistent source of ^{210}Po.

Potential pathways of contaminant exposure to human beings and other organisms include direct irradiation from gamma radiation; airborne emissions of Rn and dust (radioactive and non radioactive) and other carcinogens; and ingestion of contaminated groundwater (Berish 1990). Thus, the form that the radionuclides, particularly ^{226}Ra, occur in within phosphogypsum is of interest.

Although both Ra and Ca behave similarly chemically as both occur in chemical group IIA, it is unlikely that a solid solution of $CaSO_4$*$2H_2O$ and $RaSO_4$ occurs during the wet acid dihydrate process (Moisset 1980). This is because $RaSO_4$ crystallizes in the rhombohedric system as does barium sulphate and hemihydrate ($CaSO_4$*$1/2H_2O$), whereas gypsum ($CaSO_4$*$2H_2O$) crystallizes in the monoclinic system. In the dihydrate process the temperature is maintained below 80^oC producing gypsum directly. At higher temperature (85 to 90^oC) hemihydrate forms and solid solution formation with $RaSO_4$ is more likely. The equilibrium between $CaSO_4$*$2H_2O$ and $CaSO_4$*$1/2H_2O$ in solution is linked to temperature and the ratio of HPO_4^{2-} to SO_4^{2-}. In addition, the Ra^{2+} ionic radius (0.140 nm) is much closer to that of Ba^{2+} (0.135 nm) than to Ca^{2+} (0.099 nm). The large ionic radius difference between Ra^{2+} and Ca^{2+} hinders isomorphic substitution of Ra^{2+} for Ca^{2+} in the gypsum structure.

It may be possible for Ra^{2+} to enter the interstitial lattice positions among the water molecules of gypsum as discussed by Kushnir (1980) for Sr^{+2} and Mg^{+2}. Moisset (1980) and Moisset and Lafarge (1986) suggest that a portion of the Ra in phosphogypsum occurs as small crystals of radium sulphate. Another source of Ra in phosphogypsum is large particles of unattacked phosphate rock. Radium may also coprecipitate with barite, celestite, anhydrite, calcite or dolomite if small amounts of these are present (Langmuir and Melchoir 1985; Langmuir and Riese 1985; Miosset and Lafarge 1986). In natural ground water brines Ra concentrations were always too low to reach saturation with respect to a pure Ra phase of which $RaSO_4$ is generally the least soluble (Langmuir and Riese 1985). Instead, Ra concentrations tend to be limited by adsorption or solid solution formation or both. At low pH and high calcium concentrations, the adsorption of Ra is negligible (Langmuir and Melchoir 1985) indicating that solid solution formation is likely the major process controlling solution free ion activities of Ra in phosphogypsum pore water.

The U that remains with the phosphogypsum may be present in the residual phosphoric acid which wet the phosphogypsum (Moisset 1980) and in unattacked phosphate rock. Based on ionic radius comparisons U would be expected to substitute for Ca in $CaSO_4$*$2H_2O$. This is a similar substitution as occurs with complex salts of

U and Ca in phosphate rock but it is prevented because most U is transferred to phosphoric acid as uranium phosphate, a soluble salt in the phosphoric acid. Small amounts of U may substitute into the gypsum structure and this seems to be controlled by the redox conditions. If U is kept in a reduced form some substitution is permitted. In the presence of oxygen in the system, U(IV) tends to be oxidised to U(VI) (Baes 1956) which is more likely to move into the phosphoric acid (Hurst and Arnold 1980). Uranium levels in phosphogypsum are thus governed by the substitution of U(IV) into the crystal lattice of gypsum and by the presence of U in gypsum coated unreacted phosphate rock.

3. Pore Water Chemistry and the Prediction of Solubility Controlling Solids

i. Introduction

Pore water chemistry is of particular interest in the study of waste management because it is an indicator of the proportion of the material which is leachable and thus has the potential to be released into the aqueous environment. It is possible to predict the solubility controlling solids for major and trace elements by comparing equilibrium pore water ion activities to theoretical levels estimated from solubility constants. Pore water ion activities can be calculated from measured elemental concentrations with the use of a geochemical computer model. Solubility controlling solids if identified can serve as indicators of the maximum attainable elemental concentrations in pore water and thus they can be used in assessing the safety of inorganic waste disposal (Mattigod *et al.* 1990).

Under certain conditions the aqueous concentrations of elements can be predicted from the precipitation/dissolution reactions defined by thermodynamic data. In general adsorption processes can be overlooked in the prediction of solution concentrations produced by a solubility controlling solid if that solid has rapid dissolution/precipitation kinetics and is present in the waste or a secondary phase forms that dissolves and precipitates rapidly (Mattigod *et al.* 1990).

The hypothesis adopted for this study is that a number of the previously identified solubility controlling solids for major and trace elements in geological materials, soils and waste materials are present in phosphogypsum. There are a number of review articles, reports and books which suggest theoretical solubility controlling solids for soil and waste materials and they served as primary sources of thermodynamic information for this study (Eary *et al.* 1990; Lindsay 1979; Mattigod *et* *al.* 1990; Rai *et al.* 1984; Rai *et al.* 1987a; Rai and Kittrick 1989).

Potential solubility controlling solids are defined as likely to form within a set range of pH levels and redox conditions. Minerals which characteristically form at neutral to alkaline pH levels or in reducing conditions are not expected to be present in the phosphogypsum stack at Medicine Hat except perhaps if it interacts with the ground water which may produce saturated and thus reducing conditions near its base, or if it ages to the extent that a near neutral pH is obtained. The alkaline conditions would also be relevant if the leachate from phosphogypsum is neutralised when interacting with soils or geological materials beneath the stack. Hydroxide and carbonate solids are only expected under near-neutral to alkaline conditions while sulfides are expected only under reducing conditions. There are a number of less common minerals which also fit into one of these two groups.

ii. Chemical Properties of Phosphogypsum Pore Water

In their study of the removal of phosphogypsum waste anions by soil materials, Murray and Lewis (1985) observed that the major factor governing the F^- and PO_4^{3-} pore water activity was pH, indicating a possible precipitation effect. Fluoride likely precipitated as CaF_2 and possibly as $Ca_5(PO_4)_3F$. Phosphate may have precipitated as calcium phosphates or calcium fluorophosphates. In a noncalcareous environment $FePO_4$ formation was assumed. Sulphate activity was less dependent on pH and was assumed to be governed by calcium sulphate. In a another study where phosphogypsum was reacted with highly weathered soils, the data suggested that $AlOHSO_4$ and alunite phases could form in one of the soils studied since the solution was supersaturated relative to these two minerals (Alva *et al.* 1990). Under the same conditions, other studies have suggested the formation of basaluminite and alunite (Alva et al. 1991) or alunite alone (O'Brien and Sumner 1988).

A field study of phosphogypsum stacks in Florida, focusing on core sample analysis at different depths, indicated that none of the metallic elements would be leached from phosphogypsum (May and Sweeney 1980). Radium and U distributions in the stacks also did not suggest that leaching had occurred (May and Sweeney 1984). Using a United States Environmental Protection Agency (EPA) laboratory extraction procedure in the same study, it was observed that of the metals, Ag, As, Ba, Cd, Cr, Rb, Hg, and Se, all were present in the extract at concentrations lower than the limit set by the EPA for a hazardous toxic waste.

Fresh phosphogypsum process water in Florida had a pH level of 1.6 (Miller and Sutcliffe 1982). Dissolved Ca, Na, and SiO_2 were measured at 70, 1700, and 4700 mg L^{-1} respectively. Concentrations of solution F, P, and SO_4^{2-} were 8500, 4500, and 5300 mg L^{-1} respectively. The dissolved ^{226}Ra level was 2.0 Bq L^{-1}.

In the same Florida based study, data from ground water monitoring wells near active stacks showed elevated concentrations of Si, Na, SO_4^{2-}, F^-, hardness, PO_4^{3-}, N, Cu, Mo, Ni, and Zn (as cited by SENES 1987). Low pH values were observed in some wells due to leachate intrusion. Sulphate concentration 550 m from the phosphogypsum stack was 1750 mg L^{-1}, approximately 450 times background levels. Radionuclides in the ^{238}U chain were also elevated above background in many monitoring wells, however, all except ^{226}Ra remained at least 2 orders of magnitude below drinking water standards. Levels of ^{226}Ra were up to as high as 1.8 Bq L^{-1} within 50 to 100 m of one phosphogypsum stack. At 200 m, levels were down to 0.004 to 0.15 Bq L^{-1} which is equivalent to background.

Ground water was monitored at two active Alberta plants in Fort Saskatchewan and Calgary (SENES 1987). Levels of SO_4^{2-} were 8 to 120 times the background level with concentrations up to 12,900 mg L^{-1}. Fluoride was also high at 5 to 8 times background levels and elevated levels of N and PO_4^{3-} were present in some wells. Although the phosphogypsum pH was from 1.8 to 3.0, all ground water pH ranged from 6.5 to 8.7. Heavy metals such as Ni, Co, Cu, Mo, Fe, Zn, and Va were not significantly elevated relative to background levels.

An aged and an active stack in Canada were also studied by SENES (1987). In leachate from the active, very acidic stack (pH 3), there were elevated levels of metals including Al, Cd, Cr, Fe, Mg, Ni, and V which were attributed to low pH conditions and high solubility of metallic hydroxides. Adjacent to this site, ground water levels of SO_4^{2-}, F^-, NO_3^- and total dissolved solids (TDS) were up to one order of magnitude greater than background. Concentrations of heavy metal in leachate from the aged site with a pH of 6 were much reduced, typically substantially lower than 0.1 mg L^{-1}. Monitoring of radionuclides (Ra^{226} and Th^{228}) in dyke seepage areas at this site revealed that they did not migrate significantly.

The SENES (1987) study concluded that concentrations of the major anions such as SO_4^{2-}, Cl^-, NO_3^- and F^- are not expected to be significantly attenuated, by precipitation or solid phase surface interactions, in the absence of microbial activity. However, the movement of the major cations (Ca^{2+}, Na^+, Mg^{2+}, etc.), heavy metals and radionuclides would be expected to be significantly retarded by the attenuation properties of solute and soils.

CHAPTER III

MATERIALS AND METHODS

A. Field Sampling

Seven bulk samples of phosphogypsum, numbered samples 1 to 7, were collected within one metre of the stack surface at Medicine Hat. Samples were selected based on field pH, which was measured on location with a portable pH meter. The goal was to obtain a set of samples which would represent the range of hydrogen ion activity present at or near the surface of the Medicine Hat stack. All of the samples were obtained from three cells on the north half of the stack (Fig. 1), most being from cell 1B in the northwest corner. Samples were numbered according to the order in which they were collected. Each bulk sample was collected in a 22.7 L (5 gallon) plastic bucket which was sealed with a snap-on lid.

Bedding was observed within the material with some of the layers being distinctively black in colour in contrast to the predominantly gray matrix (Fig. 2). Thus, three smaller samples (approximately 500 g each) of the black material (samples 8-10) were collected in sealed plastic bags and included in some of the routine mineralogical and chemical analyses.

Two soil samples were collected near the site. The first came from a road cut at the level of the C horizon of an Orthic Brown Chernozem developed on glacial till (till) approximately 1 km west of the site. The second came from the level of the C horizon from the same soil subgroup but developed on sandy fluvial material (sand) and located approximately 500 m east of the site under pasture.

Upon returning to the laboratory, all samples were homogenized by stirring, and stored at 5°C. Three replicates of each sample and treatment were included in most of the analyses that follow.

B. Routine Analysis

Soon after returning to the laboratory, NH_4^+-N and NO_3^--N were extracted from subsamples of each of the soil and phosphogypsum samples using 2 M KCl as outlined by Keeney and Nelson (1982). Extracts were stored frozen to control microbial reactions (Fresenius *et al.* 1988) until analysis could be performed using a Technicon Auto Analyzer™ II. Sample 9 was not replicated. Values were expressed in mg kg^{-1} oven dry (105°C) solid.

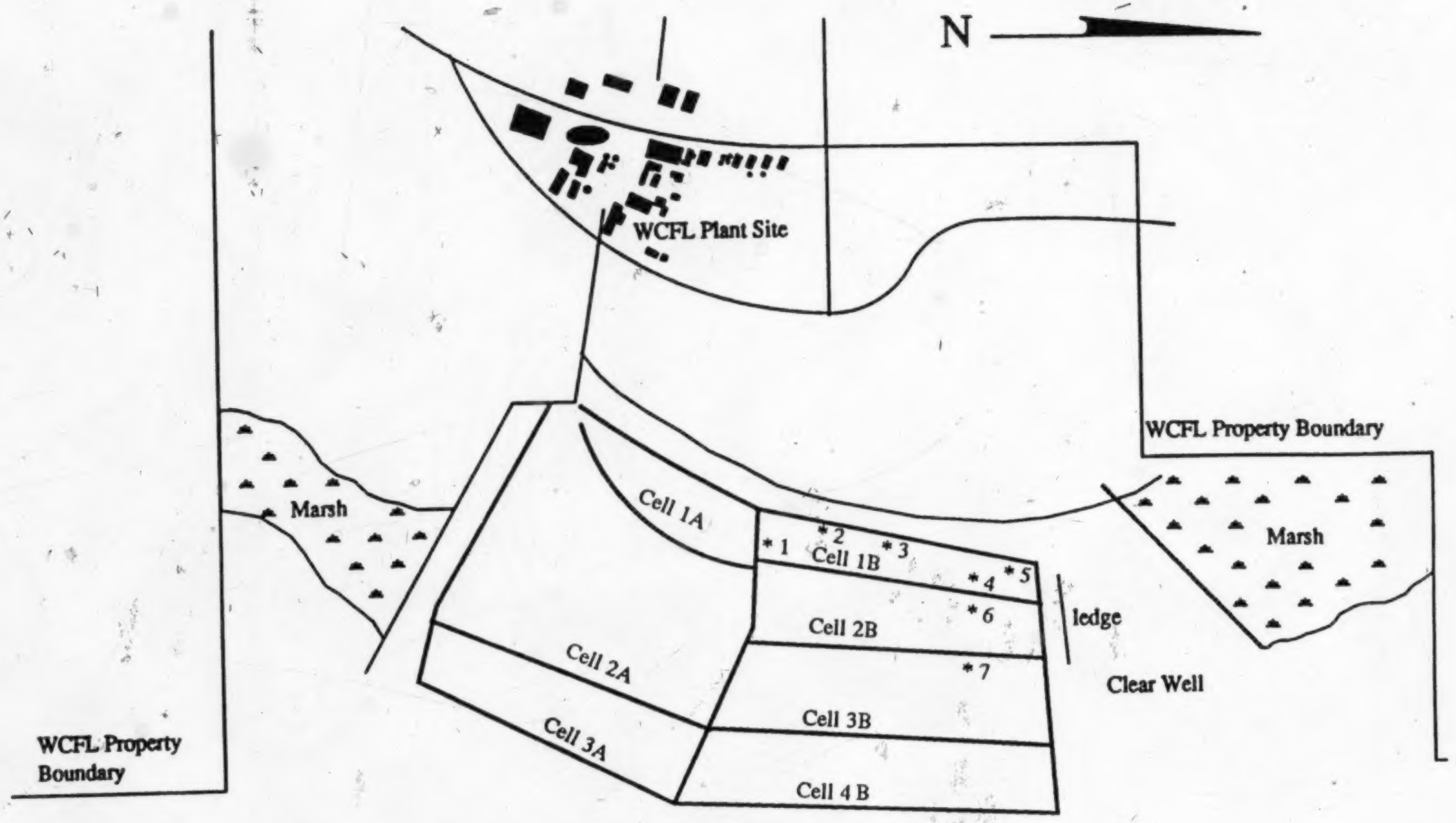

Figure. 1 Sampling locations for seven bulk phosphogypsum samples.

Approximate scale 1:14,000

(adapted from Roberts Thorne 1990)

Hydrogen ion activity was determined in 0.01 M $CaCl_2$ using the technique of Peech (1965). Replicate analyses were not carried out. For the phosphogypsum samples, 3:1 and 4:1 solution to solid ratios were included. The pH in distilled deionized water was also measured using a 3:1 solution to solid ratio. For the soil samples, 2:1 and 1:1 solution to solid ratios were included with the 0.01 M $CaCl_2$ and a 2:1 ratio was used with water.

Total cation exchange capacity was determined on phosphogypsum samples 1-8 and the two soils without replication. Cation exchange by Na^+ saturation, a technique outlined by Chapman (1965), was employed. Soils saturated with Na^+, the index ion, were rinsed with alcohol and then the Na^+ was replaced by NH_4^+. The 1 N ammonium acetate replacing solution was analysed for Na using flame atomic absorption spectroscopy.

Only the soil samples were included in the carbonate analysis as trials on phosphogypsum samples indicated that the carbonate carbon was not detectable. The technique of Bundy and Bremner (1972) was implemented.

Total C analysis of phosphogypsum samples 1-8 and the two soil samples was performed using a Leco CR12 high frequency induction furnace with infrared detection of evolved CO_2 (Tabatabai and Bremener 1970). Organic C content was calculated by subtracting carbonate C from total C content. Sample 8 was heated in muffle furnace at 450°C to observe colour changes with loss of organic matter.

Single saturated paste extracts were collected from the same set of ten samples using the technique outlined by the Richards (1954). The same manual also details the method employed for the measurement of electrical conductivity (EC). Calcium, Mg, Na and K were analysed in the extracts using flame atomic absorption spectrometry. Extract pH values were also measured. A 10-ml volume of each phosphogypsum extract and 2:1 liquid:solid pastes made with 10 g of phosphogysum, based on oven dry weight, were titrated with 0.1 N NaOH. The pH was monitored with each 0.5- to 1.0-ml addition of base to obtain a buffering curve for each extract and paste.

C. Mineralogical Analysis

1. Fractionation

Three 40-g replicates of each of the two bulk soil samples were dispersed in 400 ml of distilled water using vibration of a Braunsonic 1510 ultrasonic probe for 3 minutes at 380 watts (Edwards and Bremner 1967; Genrich and Bremner 1972). After sonification, samples were quantitatively transferred to two litre beakers. Gravity sedimentation was used to separate the clay from coarser fractions (Day 1965). The separated clay samples were flocculated by adding 1 M $CaCl_2$ and were then oven dried, weighed, and stored for subsequent analyses. The remaining soil sample was fractionated by quantitatively washing it through a 270-mesh sieve (0.05 mm) to separate sand and silt fractions which were each oven dried and weighed.

2. Clay Mineralogy

In addition to the clay separates obtained above, a second set of clay size separates were obtained through acidification with 1 N HCl to remove carbonates prior to fractionation, as described by Green (1978). Each of the clay separates was used for x-ray diffraction (XRD) analysis. This analysis was not replicated. Using the paste method of Theisen and Harward (1962), slides were prepared from calcium and potassium saturated clay separates which were rinsed free of electrolytes. The following set of clay slide pretreatments and XRD conditions were utilised (Dudas and Pawluk 1982).

1. Ca-saturated clay, equilibrated at 54% relative humidity (RH) for 24 hours and analysed at 54% RH.
2. Ca-saturated clay, equilibrated with ethylene glycol at 65°C for 24 hours and analysed under ambient conditions after equilibrating at room temperature for 12 hours.
3. Ca-saturated clay, equilibrated with glycerol at 105°C for 4 hours; after cooling, x-ray spectrum generated under ambient conditions.
4. K-saturated clay, heated at 105°C for 24 hours and analysed at 0% RH.
5. K-saturated clay, equilibrated to 54% relative humidity for 24 hours and analysed with sample chamber maintained at 54% RH.
6. K-saturated clay, heated at 300°C for 3 hours and once cooled, analysed at 0% RH.
7. K-saturated clay, heated at 550°C for 2 hours and once cooled, analysed at 0% RH.

XRD analyses were performed using a Philips PW1730 x-ray generator with a PW1710 diffractometer control, and CoKα radiation generated at 50 kV and 25 Ma. Quartz was used as an internal standard. A step scanning speed of 2 seconds for each step of 0.05^{o} 2Θ was used.

3. Phosphogypsum Mineralogy

X-ray diffractograms of bulk phosphogypsum sample 1 and black sample 8 were produced by step-scan analysis of powder mounts from 3-90^{o} 2Θ using the same diffractometer conditions as with the clay separates. Phosphogypsum phase changes on heating to 105^{o}C were examined using XRD.

D. Scanning Electron Microscopy

Selected aggregates from a surface block of phosphogypsum were examined by scanning electron microscopy (SEM). Samples were fastened to stubs and sputter coated with gold to prevent charging on the sample surface. Electron micrographs were obtained from a Cambridge Stereoscan 250 scanning electron microscope, and energy dispersive spectra providing semi-quantitative elemental compositions were produced using a Tracor Northern 5500 Energy Dispersive X-ray Analyzer with a Kevex detector. The purpose of these analyses was to examine the gypsum crystal morphology and size as well as the characteristics of any accessory minerals which could be identified and thus documented.

E. Elemental Analysis of the Solid Phase

The less-than-2-mm size fraction of the soil and bulk phosphogypsum samples including black sample 8 were air dried and analysed for the composition of 58 elements including major, trace and some rare earth elements[1]. Techniques employed included atomic absorption analysis (AA), direct current plasma-atomic emission analysis (DCP), fire assay direct current plasma-atomic emission analysis (FADCP), inductively coupled plasma-atomic emission analysis (ICP), instrumental neutron activation analysis (NA), and x-ray fluorescence (XRF) (Table 1). Pottasium hydroxide fusion dissolution was implemented for elemental analysis by DCP and HF/perchloric acid digestion was used for elements analysed by ICP or AA.

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[1] **XRAL, X-ray Assay Laboratories, a division of SGS Supervision Services Inc., 1885 Leslie Stree, Don Mills, Ontario, M3B 3J4, Canada, Tel: (416) 445-5755.**

Table 1. Methods used for the analysis of elements in the solid phase.

Element	Method[z]	Element	Method	Element	Method
Ag	ICP	Hf	NA	Sc	NA
Al	XRF	In	AA	Se	NA
As	NA	K	XRF	Si	XRF
Au	FADCP	La	NA	Sm	NA
B	DCP	Li	ICP	Sn	XRF
Ba	XRF	Lu	NA	Sr	XRF
Be	DCP	Mg	XRF	Ta	NA
Bi	ICP	Mn	ICP	Tb	NA
Br	NA	Mo	ICP	Th	NA
Ca	XRF	Na	XRF	Ti	XRF
Cd	ICP	Nb	XRF	Tl	DCP
Ce	NA	Nd	NA	U	NA
Cl	XRF	Ni	ICP	V	DCP
Co	ICP	P	XRF	W	NA
Cr	XRF	Pb	ICP	Y	XRF
Cs	NA	Pd	FADCP	Yb	NA
Cu	ICP	Pt	FADCP	Zn	ICP
Eu	NA	Rb	XRF	Zr	XRF
Fe	XRF	S	XRF		
Ge	DCP	Sb	NA		

[z] AA: Atomic Absorption Spectrometry; DCP: Direct Current Plasma Atomic-Emission Spectrometry; FADCP: Fire Assay Direct Current Plasma- Atomic Emission Spectrometry; ICP: Inductively Coupled Plasma- Atomic Emission Spectrometry; NA: Instrumental Neutron Activation Analysis; XRF: X-ray Fluorescence.

F. Radioactivity

The seven bulk refrigerated phosphogypsum samples were analysed for ^{226}Ra over a 24-hour period using an Aptec germanium gamma spectrometer with a Nuclear Data 65 multichannel analyser from which data were shunted to a personal computer. Samples were oven dried, passed through a 2-mm sieve, and packed by tapping into 170-ml polyethylene vials with screw on lids. After vials were packed to the top and the surface was smoothed, they were sealed with parafilm under the lid and were incubated for 30 days prior to analysis to ensure a sufficient period had elapsed for the establishment of secular equilibrium (Abel 1986).

After 6 months incubation at a 1:2 solid:liquid ratio, phosphogypsum samples 1 to 6 from the batch experiment were removed, filtered and extracted to remove soluble constituents by pouring five separate aliquots of distilled, deionized water over the sample, each followed by filtration under suction using a buchner funnel and #42 filter paper. The extracted phosphogypsum samples were dried separately, packed and sealed in a container, as explained above, for gamma detection after 30 days incubation.

The ^{226}Ra daughter products, ^{214}Pb (peaks 295 and 352 KeV) and ^{214}Bi (peak 609 KeV), were used to gauge the amount of ^{226}Ra present because the sum of the peak areas per unit mass for these three peaks can be directly related to ^{226}Ra levels (Bolch *et al.* 1977). The direct analysis of ^{226}Ra via its 186 KeV peak is interfered with by a peak of ^{235}U of the actinium series which also occurs at 186 KeV (Kerr *et al.* 1977). No standard for ^{226}Ra was available in our laboratory at this time. Relative ^{226}Ra levels were compared among samples and treatments using the sum of the three peak areas per gram of the daughter nuclides identified above. The comparison of batch incubated and deionized water extracted samples with untreated samples provided information on the mobility of the ^{226}Ra present in the by-product.

G. Batch Incubation

This set of experiments was undertaken in order to study the composition of pore water at or near equilibrium from phosphogypsum and phosphogypsum-soil mixes. Ion activities calculated from elemental concentrations in pore waters were used to predict solubility controlling solids present. Soil and phosphogypsum were mixed in order to examine how elements released from phosphogypsum are attenuated in a natural soil environment.

In order to obtain solution extracts, from phosphogypsum and phosphogypsum-soil mixes, with the constituents at or near equilibrium with respect to the minerals present, a set of batch incubations were designed. Incubators were 750-ml polyethylene containers with snap on lids; each lid containing a central, 1-cm diameter, circular opening. Stored refrigerated samples were passed through a 2-mm sieve and 300 g of solid, based on the oven dry weight, were combined with 600 g of distilled deionized water less that present in the sample itself. Four different mass ratios of phosphogypsum (PG) to till (S) were used: 300 g PG (PG1:S0); 272.72 g PG with 27.38 g S (PG10:S1); 150 g PG with 150 g S (PG1:S1); and 300 g S (PG0:S1). Three replicates of each treatment for each of the seven bulk phosphogypsum samples were included. The ambient temperature and pressure of 20-25^{o}C and 1 atmosphere respectively were maintained throughout the incubation. During the entire incubation, the samples were agitated daily using a milk shake mixer.

In the study of solubility equilibria, valid samples can only be obtained after the chemical system reaches a steady state, that is, the concentrations of ions or components involved in the reaction are no longer changing with time (Zachara and Streile 1990). The time required to reach a steady state can be evaluated using a kinetic study in which a batch experiment is sampled over time to determine the point at which aqueous concentrations become constant. Although some soil minerals such as gibbsite (Kittrick 1966b), kaolinite, and montmorillonite (Kittrick 1966a, 1971) can take years to confirm equilibrium, Weaver *et al.* (1971) found that most chemical parameters measured approached constant levels after 30 days in soil equilibria studies conducted over 3 months. Thus a time monitoring trial conducted over 3 months was selected for this study.

A set of independent trials with sample 1 in the PG1:S0, PG10:S1, and PG1:S1 mixes and a mined gypsum sample alone were used for the time trial in which the solution phase was extracted periodically over 90 days. The mined gypsum sample was the Satin Spar variety from East Bridgeford, England. To increase the volume of solution for multiple sampling, each time trial replicate was made up of three separate containers and a pooled sample from the three containers was obtained for each replicate sample. The mined gypsum sample was available in lower quantities and thus was made up in only one container. Time trial subsamples were removed after 1, 7, 14, 28, 60, 80, and 90 days. The long-term batch incubations were sampled at 60 and 80 days.

Immediately after mixing, sampling was performed by pouring approximately 80 g of the slurry directly into centrifuge tubes. Samples taken from 1- to 60-days of the time trial and the 60-day batch incubation samples were centrifuged at 8000 RPM with the temperature in the centrifuge ranging from approximately 10 to 20°C. The 80- and 90-day time trial samples and 80-day batch incubation samples were centrifuged at 1500 RPM with the temperature in the centrifuge in the range of 20 to 25°C. After centrifuging, the supernatant was poured off and pH was measured with a combination electrode. Samples were then passed through 0.22 micron, nylon, syringe filters and electrical conductivity (EC) was measured; most samples were then frozen until elemental analyses could be preformed. Freezing was practiced to preserve samples by minimising microbial reactions (Fresenius *et al.* 1988). Refrigeration and/or freezing are recommended methods of preservation of samples for analysis of some metals, N compounds, PO_4^{3-}, and SO_4^{2-} (Greenberg *et al.* 1985). A subsample of each of the 80 day PG1:S0 treatment samples were left unfrozen prior to elemental analyses.

The extracts were analysed for alkalinity using the technique of Bower and Wilcox (1965). Simultaneous analysis for 26 elements was performed by ICP using an ARL Model 34000 with a maxiflow torch system and GMK crossflow nebulizer with a

1200 watt power source[2]. Ammonium and nitrate nitrogen were quantified in the long-term batch extracts using a Technicon Auto Analyzer™ II.

Statistical analyses were performed using the computer program, SAS/STAT™ (Joyner 1985). Paired T tests were implemented to establish whether pore water chemical paramaters were significantly different ($P=0.05$) if the pore water was sampled at different times; if the pore water was previously frozen or left unfrozen; and in the case of ionic strength, if the chemical parameter was determined using a computer model or calculated directly from chemical measurements.

H. Computer Modelling

The data collected from the batch incubations were used to calculate the activities of ionic species with the use of a GEOCHEM-PC version 2.0 (Parker *et al.* 1990), a modified version of GEOCHEM (Sposito and Mattigod 1980), a geochemical computer model. Ion activities determined by this method can be related to theoretical levels determined from solubility constants for potential solubility controlling solids and thus can be used to predict the presence or absence of a particular solid phase. Analytical total concentrations of anions and cations including alkalinity, NO_3^--N, and NH_4^+-N along with pH and electrical conductivity (EC) (Ionic Strength (mol L^{-1}) (IS) $= 0.013$ EC (dS m^{-1})) (Griffin and Jurinak 1973) were used as input parameters. A complete set of elemental concentrations was entered into the model for each pore water extract including values that were at or near the detection limit. Although an estimate of IS and alkalinity were entered into the computer model, the model calculated IS iteratively from speciated levels of each ion and it calculated alkalinity from an assumed atmospheric CO_2 partial pressure of $10^{-3.5}$ (Bohn *et al.* 1985).

A number of the elements measured were entered in an ionized and/or complexed form and so it was assumed that all of these elements existed in the specified form in solution. Thus, As was entered as AsO_4^{3-}, B as $B(OH)_4$, Fe as Fe^{3+}, Mn as Mn^{2+}, Mo as MoO_4, Co as Co^{2+}, Cu as Cu^{2+}, Cr as Cr^{3+}, NH_4^+-N as NH_3, NO_3^--N as NO_3^-, P as PO_4^{3-}, Se as SeO_4^{2-}, S as SO_4^{2-}, and Ti as TiO^{2+}. Selenium was also modelled as SeO_3^{2-} in independent trials. In order to produce a solubility equilibria diagram for Si, it was necessary to assume that $H_2SiO_4^{2-}$ activity, the highest silica hydrogen complex in the model output, was equivalent to the activity of $H_4SiO_4^0$, the most abundant Si solution complex in the pH range of interest and the one commonly used to produce Si solubility diagrams (Lindsay 1979).

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[2] **ARC, Alberta Research Council, 250 Karl Clark Road, Edmonton, Alberta, Canada, PO Box 8330, Postal Station F, T6H 5X2, Tel: (403) 450-5111.**

The calculated ion activities were related visually to theoretical mineral solubility constants with the use of mineral isoline diagrams. The solution ion activity level is considered undersaturated relative to a potential solubility controlling solid if ion activity versus pH coordinates fall below the mineral isoline and it is considered supersaturated if these coordinates fall above the isoline. The system is at saturation relative to a mineral if ion activity versus pH coordinate values occur on the mineral isoline. A saturated condition provides indirect evidence for the presence of the mineral as a solubility controlling solid.

CHAPTER IV

RESULTS AND DISCUSSION

Laboratory and computer modelling results are presented and discussed in this chapter. The following five sections are included in accordance with the objectives of the study: A. Chemical, physical and mineralogical properties; B. Elemental chemistry of the solid phase; C. Radioactivity; D. Pore water chemistry and computer modelling; and E. Solubility equilibria relationships.

A. Chemical, Physical, and Mineralogical Properties

1. Chemical Properties

The hydrogen ion activity of both the phosphogypsum and soil samples was of particular relevance in this investigation. In a related study of phosphogypsum waste ion removal by soil minerals it was determined that, "...the pH of the system was, in general, the controlling factor in removal of the subject anions from solution due to effects on precipitation, complex formation and degree of ionization..."(Murray and Lewis 1985). Field pH values for the seven bulk phosphogypsum samples ranged from 2.5 to 5.4, whereas a narrower range was determined in the laboratory (2.6 to 4.0) where the solid to solution ratio was controlled more rigorously (Table 2). Samples 1, 4, and 6 all had a pH in water at a 1:3 solid to solution ratio near 4.0; whereas a second group of samples made up of samples 2, 3, 5, 7, and 8 were within the range of 2.6 to 2.9. Measuring the pH in 0.01 M $CaCl_2$ had no significant effect on the pH reading of the phosphogypsum samples nor did a change in the level of dilution.

Fresh phosphogypsum is acidic with a pH as low as 2.1 (May and Sweeney 1980) in an active stack which is likely due to residual phosphoric acid condensed on particle surfaces. Fluid inclusions of process acid within gypsum crystals may also occur. With ageing, the pH can rise to near neutral levels (SENES 1987). The Medicine Hat stack is only moderately aged as evidenced by the slight increase in pH corresponding to its time of ageing since plant shutdown in 1982. The pH is expected to continue to increase over time at this site.

The soil samples had pH values (in water at a 1:2 solid to solution ratio) of 8.4 (Table 2). Orthic Brown Chernozemic soils have Cca or Ck horizons and thus carbonate is present (Agriculture Canada Expert Committee on Soil Survey 1987). The pH of calcareous soils when measured in the laboratory is typically around 8.3, if

Table 2. Routine chemical properties of soil and phosphogypsum samples.

	Phosphogypsum Sample #											Soil	
Parameter	1	2	3	4	5	6	7	8	9	10	Mean[z]	Sand	Till
Field pH	5.4	3.0	2.7	3.8	2.5	4.4	3.5	§	§	§	3.6	§	§
pH H_2O 1:3[y]	4.0	2.6	2.8	4.0	2.8	3.9	2.9	2.6	§	§	3.3	8.4	8.4
pH $CaCl_2$ 1:3[x]	3.6	2.6	3.0	3.8	2.7	3.9	2.6	2.5	§	§	3.2	7.8	8.2
pH $CaCl_2$ 1:4[w]	3.8	2.7	2.9	3.6	2.9	3.6	3.8	2.7	§	§	3.3	7.7	8.2
CEC (cmol(+)/kg)[v]	4.2	6.7	8.3	4.7	5.2	4.5	6.2	9.5	§	§	5.7	5.7	11
NH_4^+-N (mg/kg)[u]	14.0	252	280	7.00	140	10.5	140	196	84.0	1260	121	2.66	3.22
NO_3^--N (mg/kg)[u]	0.84	42.0	85.4	0.56	16.8	0.70	7.42	29.4	2.66	266	22.0	0.98	5.46
Organic C (%)	0.11	0.18	0.22	0.08	0.32	0.17	0.64	1.23	§	§	0.25	0.51	0.35
$CaCO_3$-C (%)	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	§	§	ǂ	0.55	1.01

[z] denotes mean of 7 bulk phosphogypsum samples; [y] 1:3 solid to H_2O ratio (soil 1:2); [x] 1:3 solid to 0.01 M $CaCl_2$ ratio (soil 1:2); [w] 1:4 solid to 0.01 M $CaCl_2$ ratio (soil 1:1); [v] cation exchange capacity; [u] 2 M KCl extractable; ǂ denotes content below detection limit; § denotes data unavailable.

exchangeable sodium is low (Bohn *et al.* 1985). The pH can be elevated in the presence of high levels of Na^+ and more rarely K^+. Generally when the mass of $CaCO_3$ in soils exceeds several percent, it controls both soil pH and soil solution Ca^{2+} concentrations (Sposito 1989). For both soil samples the pH was slightly lower in 0.01 M $CaCl_2$ indicating the presence a small amount of exchangeable H^+. There was no noticeable effect of dilution.

The total cation exchange capacity (CEC) of the phosphogypsum samples ranged from 4.2 to 9.5 cmol (+) kg^{-1}; all but two of the samples were in the 4.2 to 6.7 cmol (+) kg^{-1} range (Table 2). Sample 8 had the highest CEC: 9.5 cmol (+) kg^{-1}. The CEC in the phosphogypsum was expected to be very low as there was little or no organic matter or phyllosilicates present. Part of the CEC detected may have been due to interference from Na present in the phosphogypsum itself. This is supported by saturated paste extract data as samples 2, 3, and 8 which had relatively high levels of soluble Na (Table 3), also had the highest CEC levels. The sand sample had a CEC near that of the phosphogypsum at 5.7 cmol (+) kg^{-1}. The till sample had a CEC nearly twice this level at 11 cmol (+) kg^{-1}. The CEC values of the phosphogypsum and soil samples are quite low as they occur within the low range found in pure kaolinite of 2-16 cmol (+) kg^{-1} (Hausenbuiller 1985).

Extractable NH_4^+-N and NO_3^--N levels in ten phosphogypsum (three black) and two soils were presented in Table 2. In a study by Malhi *et al.* (1985) on mineral N at 100 cultivated sites in north central Alberta, the extractable NH_4^+-N was up to 16 mg kg^{-1} soil while the NO_3^--N was up to 65 mg kg^{-1}, assuming a hectare furrow slice is equivalent to 2 million kilograms. More than half of the phosphogypsum samples were elevated relative to NH_4^+-N values for north central Alberta soils. The levels were from 5 to 80 times greater, with sample 10 showing the highest level of enrichment. Most of the NO_3^--N measurements in the phosphogypsum were at or below the maximum found in northern Alberta soils. Only sample 10, a black surface crust sample, showed significant enrichment over soil with NO_3^--N levels 4 times higher. The soil samples were much lower in NH_4^+-N and NO_3^--N than surface horizons in north central Alberta.

These results indicate that at least in some areas of the stack there are significant levels of enrichment of NO_3^--N and particularly NH_4^+-N. The relatively mobile NO_3^--N is a potential pollution hazard to surface and ground waters (Bohn *et al.* 1985). Nitrate nitrogen is regulated in Canadian drinking water at a maximum level of 10 mg kg^{-1} (Federal-Provincial Subcommittee on Drinking Water 1989) as it can be implicated in fetal methemoglobinemia which requires the conversion of NO_3^- to NO_2^-

Table 3. Chemical properties of saturated paste extracts.

Parameter	Phosphogypsum Sample #									Soil	
	1	2	3	4	5	6	7	8	Mean^z	Sand	Till
Moisture Content (%)	84	76	72	110	88	69	80	83	86	23	26
EC (dS/m)	2.1	9.4	12	2.0	6.8	2.0	5.4	6.5	5.7	0.8	11
Ca (mg/L)^y	280	880	1800	670	870	690	1300	1000	930	33	360
Ca (mmol/kg)^x	5.9	17	32	19	19	12	26	26	19	0.2	2.3
K (mg/L)	5.2	750	1100	8.5	470	5.8	540	510	410	5.5	48
K (mmol/kg)	0.1	14	20	0.2	10	5.8	11	14	8.7	╪	0.3
Mg (mg/L)	1.8	140	140	0.6	140	2.5	100	210	75	30	140
Mg (mmol/kg)	0.1	4.4	4.2	╪	3.6	0.1	1.8	9.0	2.0	0.3	1.5
Na (mg/L)	9.0	1000	1000	6.8	530	10	340	700	410	3.2	480
Na (mmol/kg)	0.3	33	31	0.3	20	6.9	12	32	15	╪	6.0

^{z} denotes mean of 7 bulk phosphogypsum samples; ^{y} expressed per volume of extract; ^{x} expressed per mass of solid used to generate the extract; ╪ denotes content below detection limit.

and the loss of effective hemoglobin through its conversion to methemoglobin (DeZuane 1990).

Organic C levels in most of the phosphogypsum samples were comparable to the levels found in the C horizon samples (Table 2). All but one sample were less than 1% organic C which for comparison is the minimum organic C requirement for a Chernozemic A horizon (Agriculture Canada Expert Committee on Soil Survey 1987). Sample 8, a black sample, had an organic C level of 1.23% and an organic matter level, calculated from the organic C (Agriculture Canada Expert Committee on Soil Survey 1987), of 2.2% which is comparable with organic matter levels found in Phosphoria phosphorite (Gulbrandsen 1966). The dark colouration was confirmed to be related to organic content by heating sample 8 in a muffle furnace at 450°C to release all organic C which turned the sample colourless.

It is likely that the residual enrichment in organic matter in localized layers within the stack originates from organic components of the phosphate rock itself (Fig. 2). Vick (1977) attributed colour differences which result in a banded or layered appearance in another phosphogypsum stack to changes in the calcining process, and differences in colouration were not associated with measurably different gradation, mineral constituents or engineering properties.

Since the pH of the phosphogypsum samples did not exceed 4, carbonate minerals were not expected to be present since they are highly soluble and thus generally unstable under acidic conditions (Lindsay 1979). Trials with phosphogypsum samples indicated that there was no detectable carbonate C. The soil samples were enriched in carbonate with the sand containing 0.55% carbonate C and the till containing 1.01% carbonate C (Table 2). Because the carbonate content in these soils is several percent, it is expected to control both soil pH and soil solution Ca^{2+} activities (Sposito 1989). The remainder of the total C in the soils was attributed to organic C which was 0.51% for the sand and 0.35% for the till.

Analytical data included in Table 3 from the phosphogypsum saturated paste extracts for electrical conductivity (EC); concentration of Ca, K, Mg, and Na; and pH indicated an extremely high degree of variability with coefficients of variation of over 80% in the case of K. Even Ca levels were quite variable with a coefficients of variation near 50%. This degree of variability, particularly for Ca, is somewhat surprising since if the solution Ca^{2+} activity is at equilibrium with gypsum, one would expect that Ca concentration would not vary a great deal. This requires the assumption that ionic strength and the concentration of other major ions is consistent among samples.

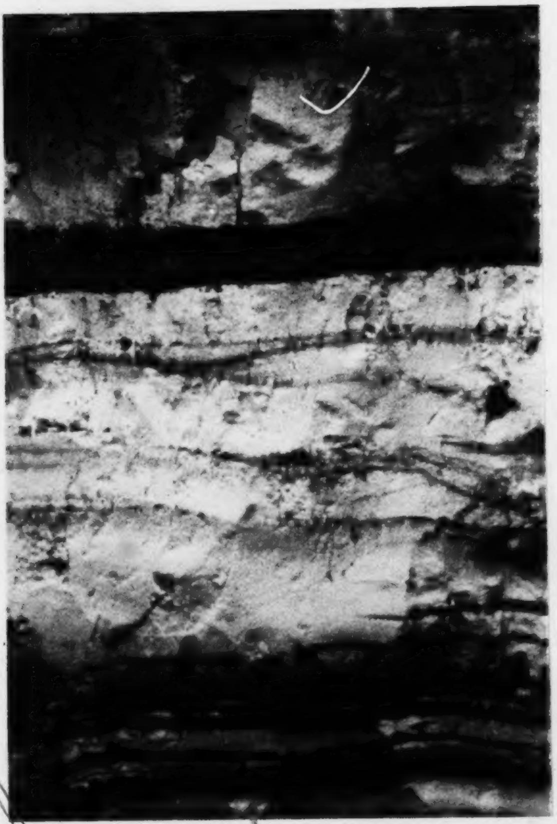

Figure 2. Field profile of phosphogypsum stack showing bedding (depth from surface to approximately 0.5 m).

A number of factors may render the assumptions regarding solution stability invalid. It is expected that the system had not reached a steady state equilibrium as pastes were only maintained for one to two hours prior to filtration permitting such factors as moisture content to have an effect on solution composition; this helps explain some of the variability. It has been noted that if a soil contains gypsum, the conductivity of a saturation extract can increase as much as 1 or 2 dS m^{-1} upon standing (Richards 1954). Another source of variation is pH and it is evident that the distributions of sample EC, and concentrations of the four elements varied inversely with pH. This can be attributed to the dependency of the solubility of a number of minerals on pH. For example, in the case of apatite minerals, their solubility varies inversely with pH (Lindsay 1979) so that higher solution concentrations of P are expected at lower pH. Phosphate anions react with cations stimulating a release of cations from the solid phase to maintain equilibrium with the specific free ion activity. Total solution concentrations of an ion include the free ion as well as the concentrations of complexes. This short term study of saturated pastes reveals that although phosphogypsum is generally a very pure material it has a complex chemistry which warrants a more intensive study of equilibrium conditions.

The till sample had a greater level of all saturated paste extract parameters than the sand sample, and the till extract had the highest electrical conductivity of all of the samples while the sand sample had the lowest (Table 3). This may be related to higher cation exchange capacity and carbonate in the till compared to the sand.

Titrations of 10 g of each phosphogypsum sample in 20 ml of water and of 10 ml of saturated paste extract with 0.01 M NaOH revealed a buffering effect in most samples of both the slurry and extract between pH 6 and 8. Slurry samples of 1, 4, and 6 required only up to 0.5 mmol NaOH to reach a pH near 10 while slurry samples 2, 3, 5, 7, and 8 required from 1.0 to 1.8 mmol NaOH to reach a pH greater than 10. Figures 3 and 4 show the titration curves of a sample from each group (samples 5 and 6) with the remaining curves being included in Appendix I. The variation in approximately one pH unit between these two groups of samples, due to differences in the level of phosphoric acid present, could account for the differences. Similar trends were observed among the saturated paste extract titrations.

It is likely that phosphoric acid is the dominant acid present in the material. The buffering effect observed between pH 6 and 8 in most titrations corresponds to the second pK_a of phosphoric acid at 7.199 while its other two pK_a values occur out of the pH range examined at 2.148 and 12.15 (Harris, 1987).

During the titration of the saturated paste extracts a small amount of gypsum

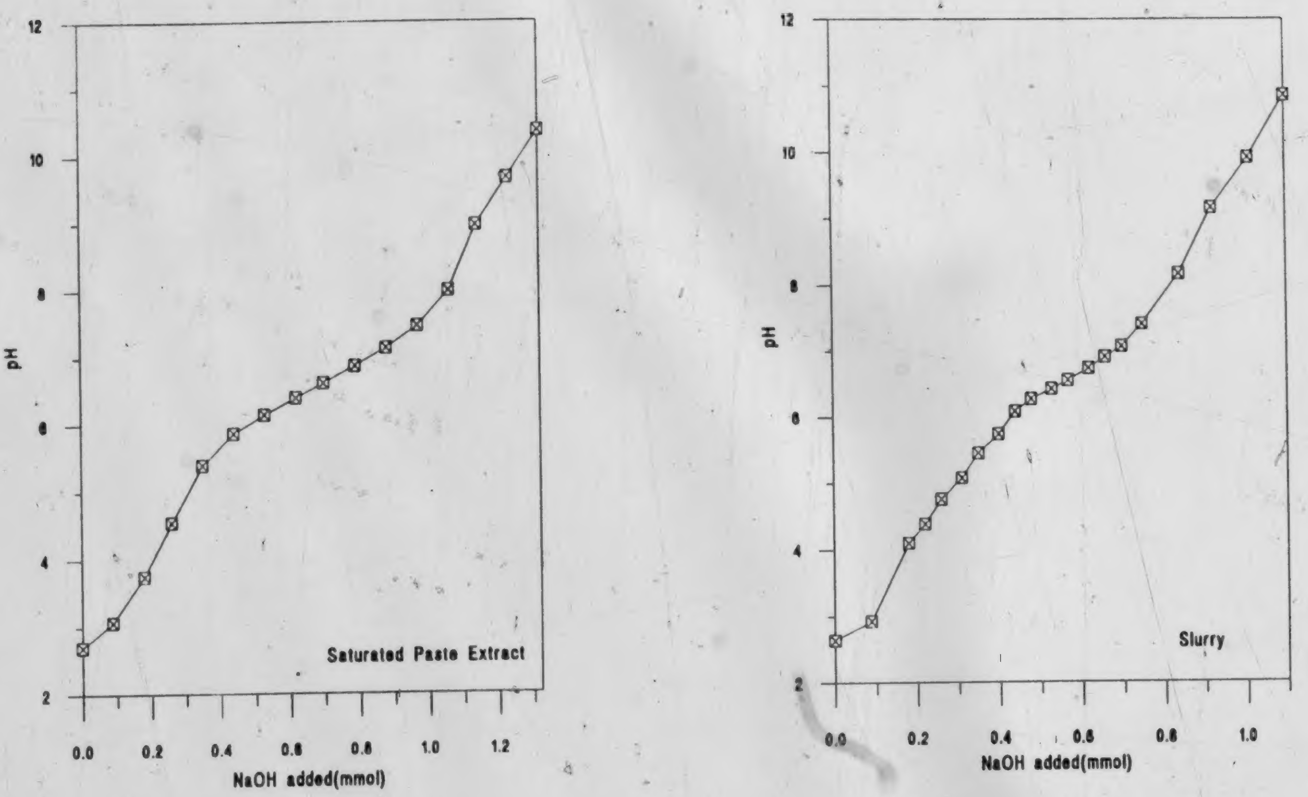

Figure 3. Base titration of phosphogypsum sample 5.

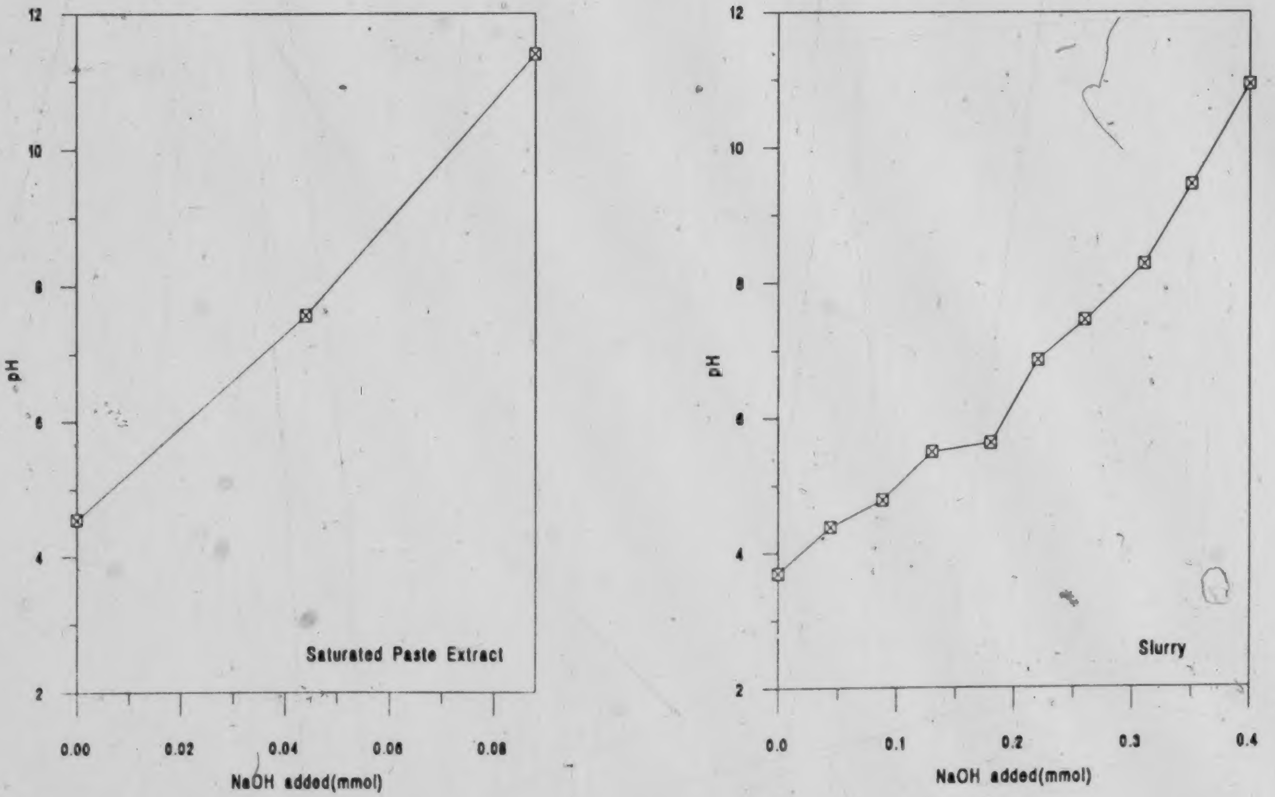

Figure 4. Base titration of phosphogypsum sample 6.

precipitate was observed to form which was identified using x-ray diffraction. This phenomenon was attributed to an increase in the free ion activity of SO_4^{-2} (confirmed by speciation calculations using GEOCHEM) at the expense of HSO_4^- and H_2SO_4 as the pH increased thus releasing a small amount of free SO_4^{2-} to react with Ca^{2+} and H_2O forming gypsum.

2. Physical Properties

The till sample had a loam texture made up of 55% sand, 31% silt and 14% clay. The percentage clay present corresponds to the CEC of 11 cmol (+) kg^{-1}. If pure montmorillonite is assumed to have a CEC of 100 cmol (+) kg^{-1}, the clay is assumed to be the only soil component active in CEC, and the other clay components, likely dominated by mica and kaolinite (Dudas and Pawluk 1982), are considered to have CECs averaging 15 cmol (+) kg^{-1}, then the proportion of montmorillonite in the sample should be approximately 11% and the proportion of other clay minerals, 3.2%. The sand sample was classed in the sand textural group because it contained 94% sand, 4.6% silt and 1.5% clay.

The phosphogypsum samples were not fractionated due to solvination and flocculation during gravity sedimentation assays (Doner and Lynn 1989). Particle size and form were observed using the scanning electron microscope. Gypsum has a monoclinic crystal system and crystals are typically tubular or needle-like (Doner and Lynn 1989). However, the larger crystals of phosphogypsum observed under the scanning electron microscope (SEM) were tabular in shape (Fig. 5) with sides that typically ranged from 15 to 30 μm, a thickness from 3 to 5 μm and a maximum length from 20 to 40 μm. Solid needle shapes, hollow four-sided tubular shapes and thin flakes were also observed. All crystals examined fell in the silt size range. It is estimated from Figure 5 that up to 70 percent of the phosphogypsum falls in the coarse silt class (20 to 50 μm) and is tabular while the remainder, made up of finer tubes, needles or flakes and less distinctive forms can be classed in the medium to fine silt range (2 to 20 μm). Others have described phosphogypsum as a granular material with a grain size distribution ranging from sand with a trace of silt to silt with a trace of clay (SENES 1987). In geotechnical terms these researchers classed the by-product as an inorganic non-plastic silt or sandy silt. With the use of wet sieve analysis, Blight (1969) classed the material in the silt sized range. Most of the crystals distributed between 10 and 50 μm in the particle size analysis reported by Vick (1977).

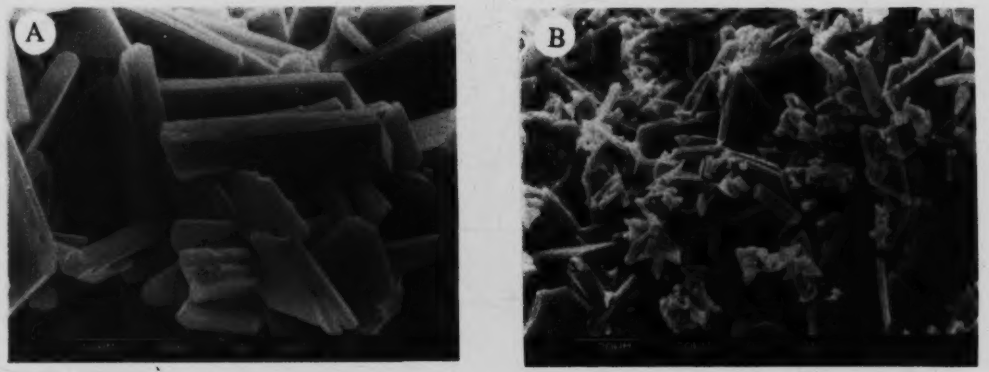

Figure 5. Micrographs of the phosphogypsum matrix dominated by well formed gypsum crystals. A, high magnification showing crystal morphology. B, lower magnification showing particle size.

3. Mineralogical Properties

i. Soil Clay Fractions

In general the diffractograms produced for the till and sand clay separates correspond closely to those described by Dudas and Pawluk (1982) for southern Alberta soils. Without the removal of carbonate prior to analysis, the K saturation was evidently not complete due to the presence of a large 1.4-1.5 nm peak for the 105°C, 0% relative humidity (RH) treatment (Fig. 6 and 8). The presence of carbonate in the separates was evidenced by a peak at 0.303 nm. The Ca saturated treatments for both the samples with carbonate and without carbonate corresponded closely in the distribution of peaks although the d-spacing was generally slightly higher when the carbonate was not present by up to 0.2 nm (Fig. 6-9).

Peaks at approximately 0.426 and 0.335 nm were attributable to quartz, although there may be some overlap with second order phyllosilicate peaks (Fig. 6-9). Small perturbations at less than 0.5 nm may also indicate the presence of clay sized feldspar.

Due to the problem with the K saturated pretreatment, the samples with the carbonate removed were used to determine the suite of clay minerals present (Fig. 7 and 9). Both soil samples were rich in smectite, specifically montmorillonite. Beidellite which has previously been identified in southern Alberta soils (Dudas and Pawluk 1982), was not discernable as no 1.5 nm peak was evident with glycerol saturation. Kaolinite followed smectite in abundance in these samples followed by mica including muscovite and possibly biotite. Chlorite was fourth in abundance, its positive confirmation apparent from the near 1.4 and 0.7 nm peaks evidenced in the K saturated, 550°C, 0% RH treatment.

It is possible that vermiculite is present in these samples although Dudas and Pawluk (1982) did not observe this mineral in similar clay separates. Under the glycerol treatment its first order peak would interfere with the chlorite first order peak near 1.4 nm, which is evident as a small shoulder on the smectite peak (Fig. 7 and 9). Some evidence for its presence is that apparently not all collapsed layers rehydrated when K saturated specimens were heated at 105°C and equilibrated at 54% RH since the ratio of intensity of the 1.0 nm and 0.7 nm peaks was less than the same peak ratio for the Ca saturated 54% RH equilibrated samples.

Clay separates from this region typically contain about 51 to 54% smectite, 29% mica, and the remaining 17% is dominated by kaolinite (Dudas and Pawluk

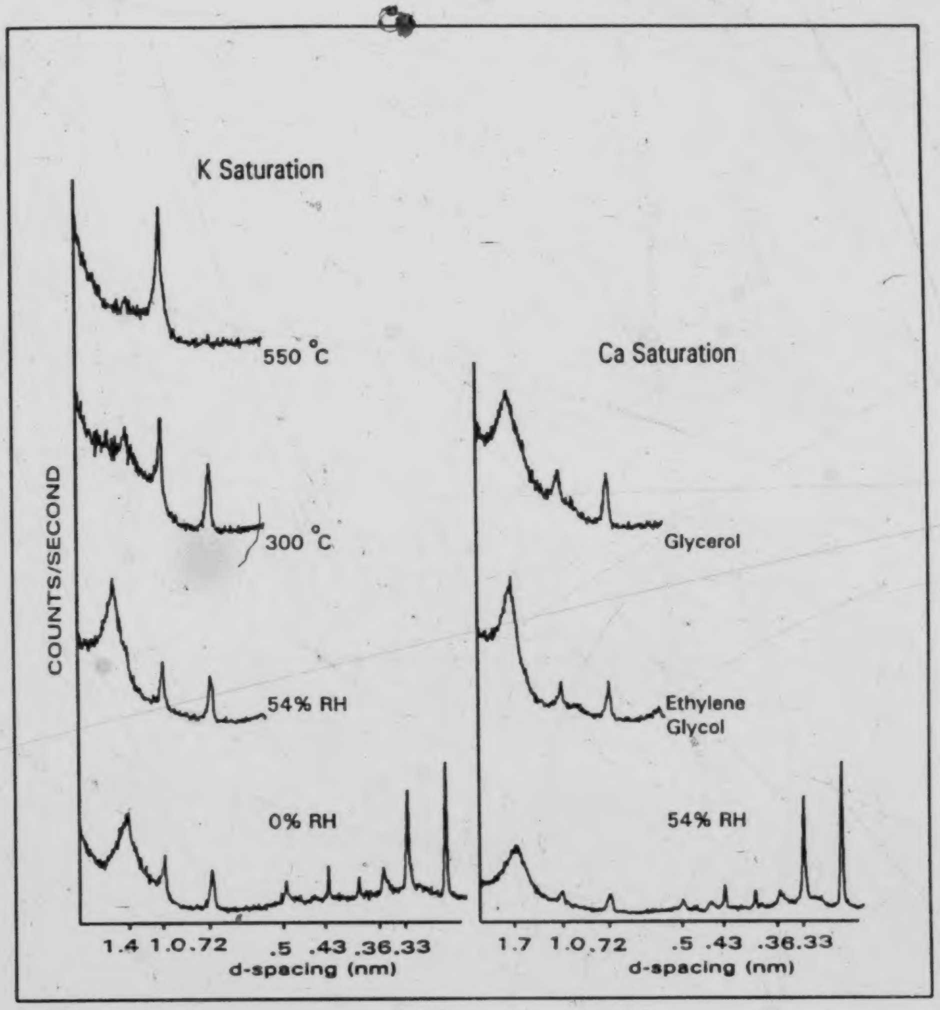

Figure 6. X-ray diffractogram of clay separate from sand sample.

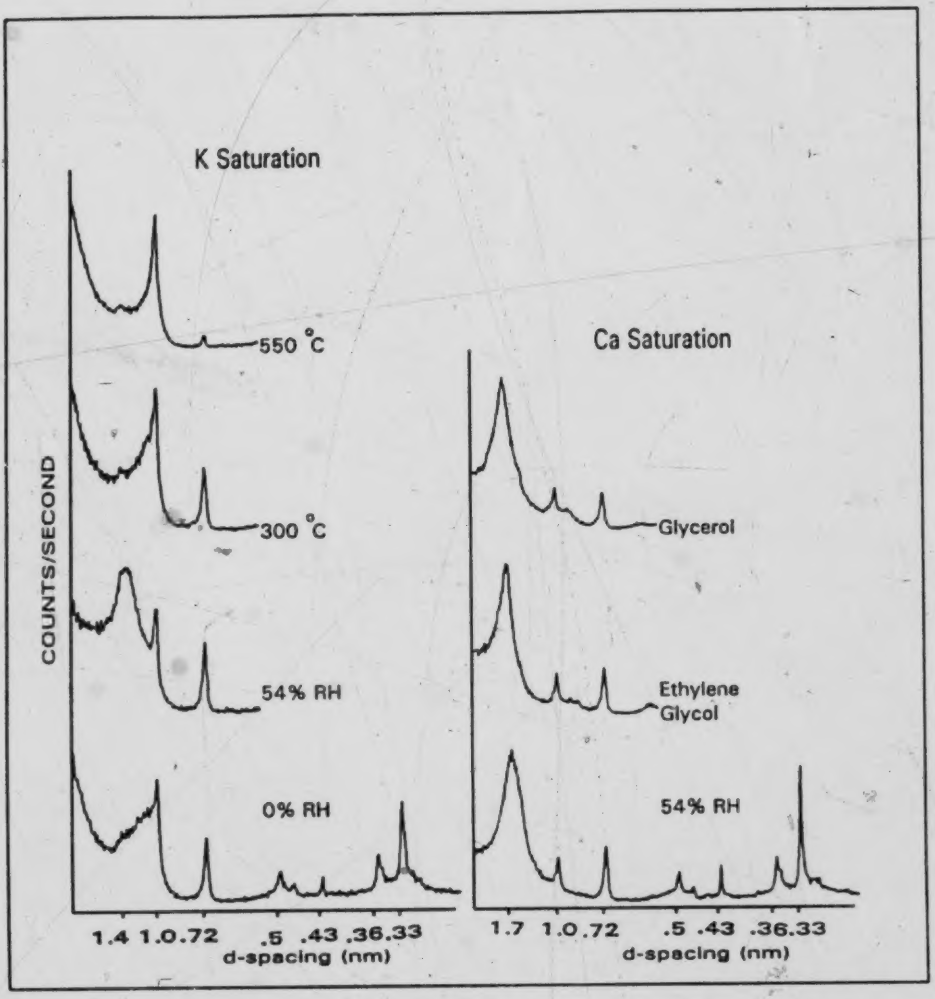

Figure 7. X-ray diffractogram of clay separate from sand sample with $CaCO_3$ removed.

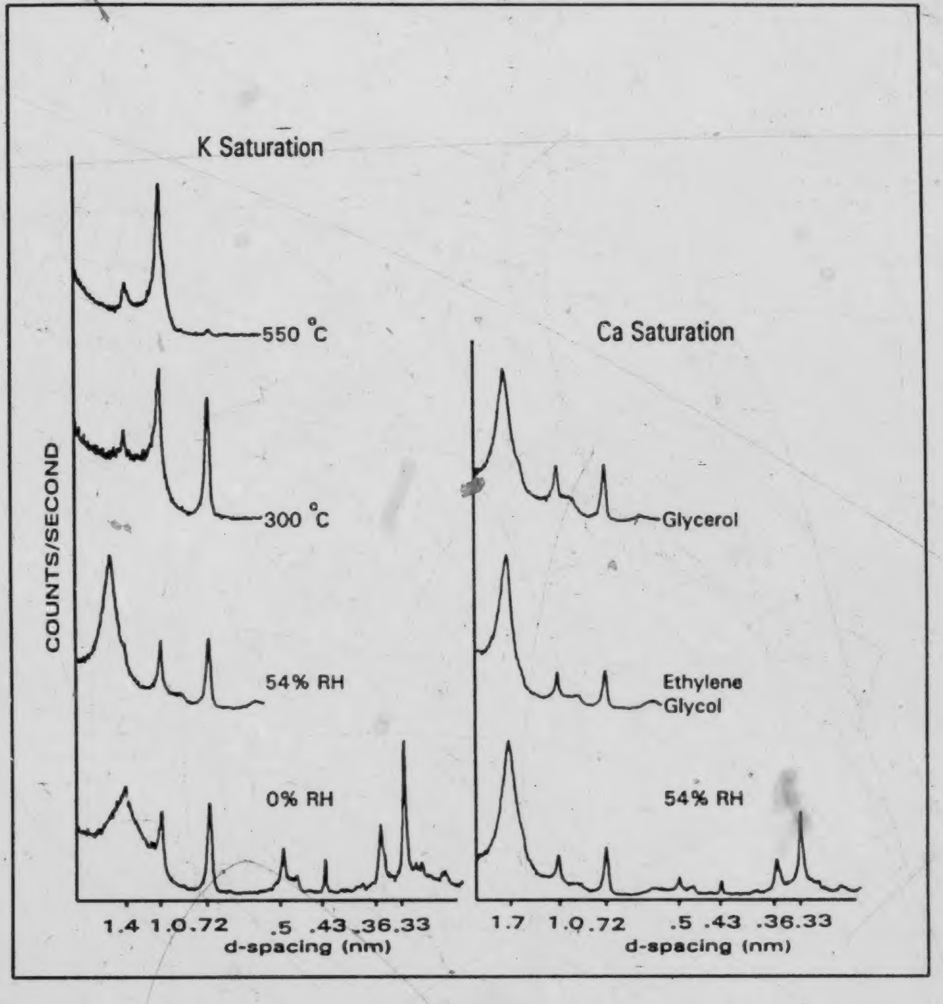

Figure 8. X-ray diffractogram of clay separate from till sample.

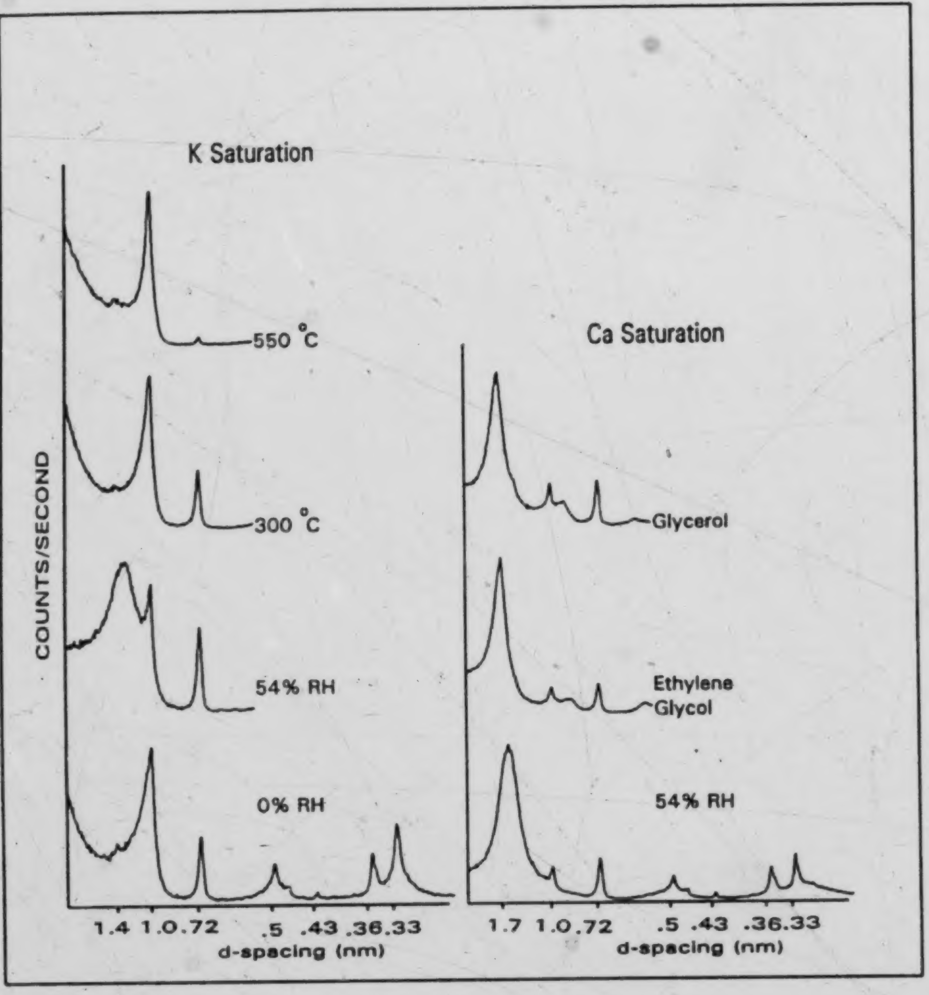

Figure 9. X-ray diffractogram of clay separate from till sample with $CaCO_3$ removed.

1982). For the samples in this study, the three most abundant minerals were consistent with the earlier study but the kaolinite was present at slightly greater levels than the mica. The smectite appeared to be present at comparable levels.

ii. Phosphogypsum

X-ray diffraction of phosphogypsum powder mounts from samples 1 and 8 was in agreement with the earlier work of May and Sweeney (1980) confirming that the material is dominated by gypsum with the quartz being the only other mineral detectable by this method. The black sample 8 had similar mineralogy to the lighter coloured sample 1. Quartz likely occurs at levels between 5 and 10% in the material. Diffractograms generated at 30°C, 45°C, 60°C, 90°C, and 105°C of powder mounts produced from sample 1 indicated that the transformation to hemihydrate or bassinite ($CaSO_4 * 1/2H_2O$) was occurring once the temperature reached 90°C. This study was necessary as some data are expressed in this thesis per mass of oven dry (105°C) solid and are thus in fact standardized to hemihydrate. For a quick short hand conversion from a hemihydrate to a gypsum content, not accounting for impurities present, one can multiply by 0.84.

Using energy dispersive x-ray analysis with scanning electron microscopy (SEM), among the matrix of the well-formed gypsum crystals, crystal or amorphous materials were located which were dominated by Si and/or P combined in some cases with significant amounts of Na, K, Ca and/or S (Fig. 10 and 11). The Au on these spectra is a remnant of the Au sputter coating which must be put in place prior to viewing to avoid charging on the surface of the material.

In Figure 10A the pitted central crystal is predicted to be quartz due to the dominant Si peak on the energy dispersive spectrum. The S and Ca peaks on the spectrum are due to the gypsum in the background. The quartz appears pitted from weathering likely due to the acid treatment of the phosphate rock during processing.

Silica rich areas were frequently encountered within the samples examined. A crystal (Figure 10B) was located which was rich in Si, Al and Na with background levels of S and Ca. This could be any number of minerals but is likely a Na rich feldspar of the plagioclase solid solution series. Plagioclase feldspars are ubiquitous in nature making up nearly a third of the earth's crust (Ahrens 1965) and feldspars accumulate in sedimentary environments as a weathering residue of igneous and metamorphic rocks (Rankama and Sahama 1950; Mason 1966).

Areas rich in P were also located which were accompanied by Ca, K, Si, S and

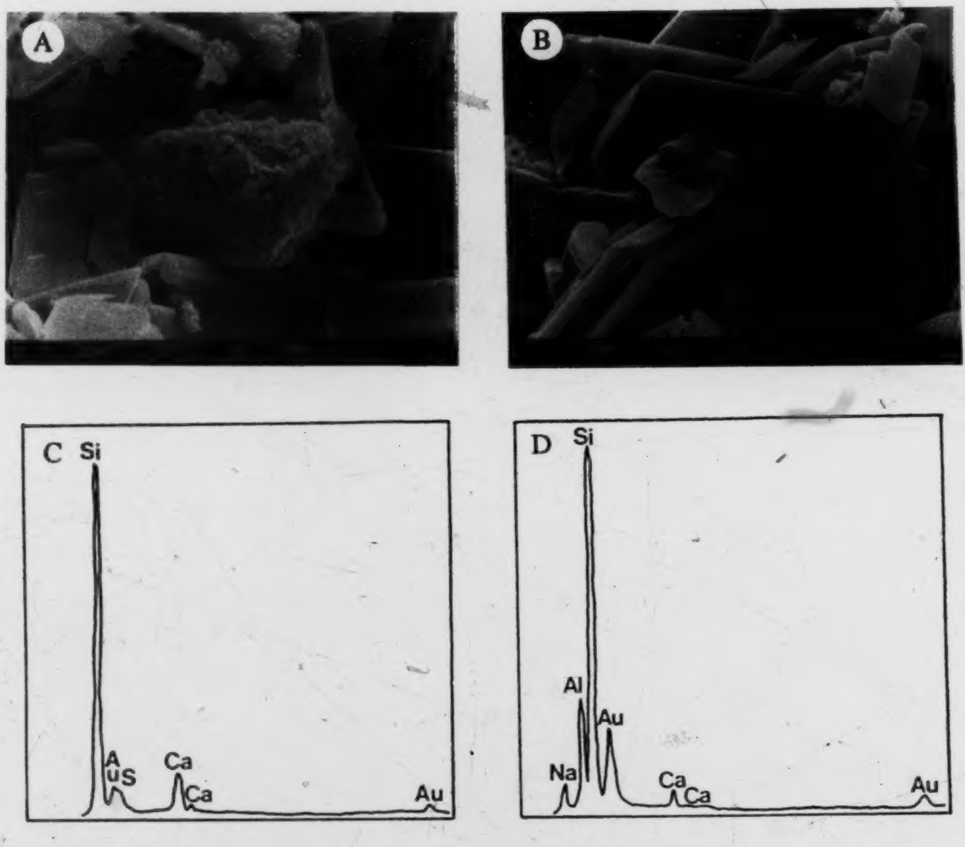

Figure 10. Micrographs of accessory minerals in phosphogypsum. A, a pitted quartz grain. B, a sodium silicate grain assumed to be a sodium feldspar. C and D, energy dispersive spectra for A and B respectively.

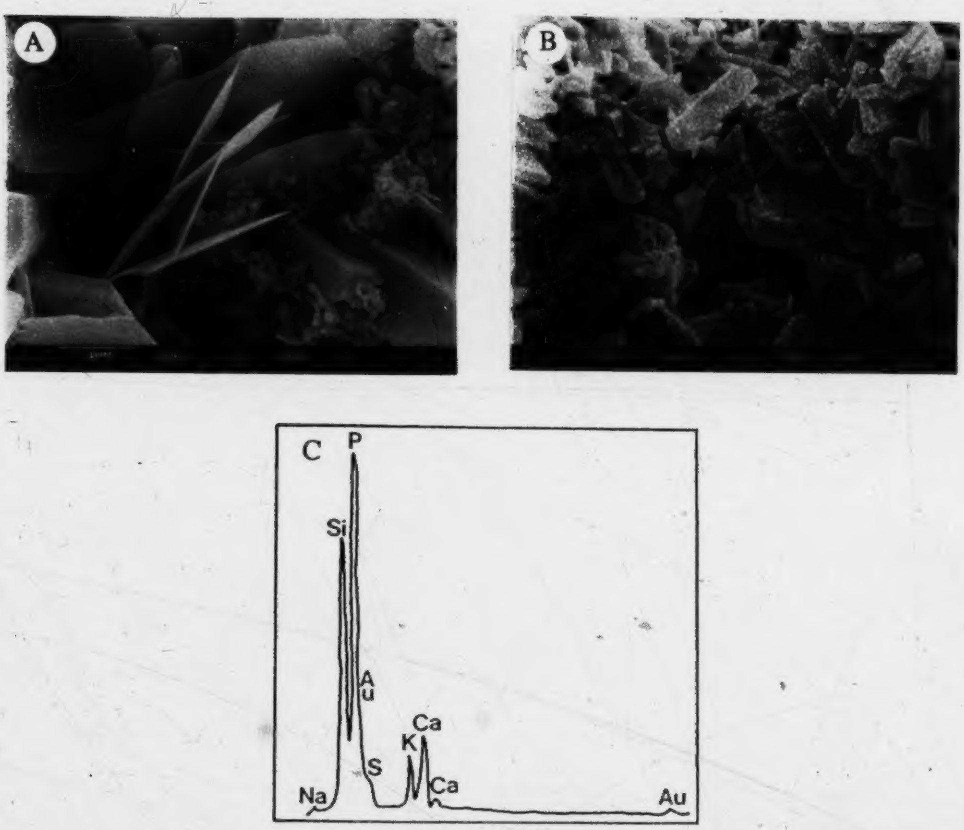

Figure 11. Micrographs of a phosphorus rich area. A, area under high power. B, area under lower power in bottom left corner within the gypsum matrix. C, energy dispersive spectrum.

trace levels of Al and Na (Figure 11). It is predicted that the main mineral present is an apatite, likely fluorapatite which may contain trace levels of K and Na substituting for Ca (Cathcart 1980). Some of the Ca and S is likely due to background gypsum and the Si peak is likely background quartz or in combination with Al and possibly K, a phyllosilicate such as muscovite or an alkali feldspar.

B. Elemental Chemistry of the Solid Phase

In general the distribution of elements in phosphogypsum, excluding S and P, follows the same relative trends observed in average phosphate rock with only the same few elements in each showing significant (at or near an order of magnitude) enrichment over average shale or crustal rocks (Tables 4-6). With few exceptions the soils were measured to have elemental distributions comparable to average shale, crustal rocks and other soils.

The elements have been divided into three groups: major elements, trace elements and rare earth elements to describe these trends. Elemental contents have been compared with average world shale values (Krauskopf 1979), average world crustal abundances and with typical soil levels (Sposito 1989). Shale serves as an important standard because shale is the most common form of surface rock and thus indicates typical background levels at or near the surface of the earth (Altschuler 1980). An elemental enrichment in phosphogypsum relative to shale is an indication of a potential for surface contamination with this element.

1. Major elements

Oxides of Al, Fe, K, Mg, Na, Si and Ti are depleted in both phosphate rock and phosphogypsum relative to shale, crustal rocks and soil values with the phosphogypsum showing depletion by several orders of magnitude in the oxides of Al, Fe, K, and Na (Table 4). Samples 7 and 8 are slightly elevated relative to the other samples in the oxides of Al, K, Si and Ti. Phosphogypsum is significantly enriched in SO_3 relative to shale while phosphate rock is only slightly enriched in SO_3; the reverse is true in the case of P_2O_5. Notably, phosphogypsum contains less than 2% P_2O_5 compared to a near 30% level in phosphate rock. Although not measured in this study, a typical F level for phosphogypsum produced by the dihydrate process is 1.2% (Kouloheris 1980) which is 20 times in excess of shale levels of 0.06% (Krauskopf 1979).

Table 4 . Total content (%) of major elements in phosphogypsum and soil samples and literature values for terrestrial material.[z]

	Phosphogypsum Sample #									Soil						
Element	1	2	3	4	5	6	7	8	Mean[y]	Sand	Till	PR[x]	Crust[w]	Shale[w]	Soil[v]	EF[u]
Al_2O_3	0.18	0.17	0.22	0.13	0.24	0.17	0.55	0.49	0.24	5.08	8.56	1.75	15.3	17.4	13.6	0.01
CaO	30.0	29.4	29.2	31.6	31.8	31.4	27.7	28.9	30.2	3.73	4.63	43.8	5.74	3.5	3.50	8.6
Fe_2O_3	0.03	0.03	0.06	0.03	0.04	0.02	0.05	0.07	0.04	1.95	2.56	1.09	8	6.72	3.72	0.01
K_2O	0.04	0.05	0.08	0.02	0.05	0.03	0.16	0.14	0.06	1.18	1.66	0.46	2.53	3.01	1.81	0.02
MgO	0.39	0.41	0.41	0.41	0.42	0.42	0.38	0.38	0.41	0.60	1.94	0.36	3.81	1.49	1.49	0.27
Na_2O	0.05	0.07	0.08	0.02	0.04	0.03	0.08	0.07	0.05	1.14	1.56	0.68	3.24	1.21	1.62	0.04
P_2O_5	1.29	1.34	1.37	0.78	1.23	1.57	1.29	1.35	1.27	0.11	0.12	29.8	0.25	0.1	0.1	13
SiO_2	7.11	5.25	5.38	4.41	5.85	6.55	10.1	12.2	6.38	81.9	71.2	12.3	60.3	50.9	66.3	0.12
SO_3	64.4	65.2	63.3	68.6	65.9	65.2	59.6	52.9	64.6	0.26	0.93	2.17	0.07	0.62	0.4	104
TiO_2	0.07	0.06	0.06	0.04	0.07	0.05	0.10	0.13	0.06	0.15	0.35	0.15	0.83	0.48	0.48	0.14
LOI[t]	21.0	25.8	28.7	22.0	26.3	21.2	31.2	35.1	25.2	4.16	7.77	§	§	§	§	§

[z] detection limit at 0.01% except SO_3 at 0.025%; [y] denotes mean of 7 bulk phosphogypsum samples; [x] Meade Park phosphate rock (PR) taken from Gulbrandson (1966); [w] taken from Krauskopf (1979); [v] taken from Sposito (1989); [u] EF = mean phosphogypsum content/shale content; [t] loss on ignition at 450°C; § denotes data unavailable.

Table 5 . Total content (mg/kg) of some trace elements in phosphogypsum and soil samples and literature values for terrestrial material.

Element	DL^z	Phosphogypsum Sample #								Mean^y	Soil		PR^x	Crust^w	Shale^w	Soil^v	EF^u
		1	2	3	4	5	6	7	8		Sand	Till					
Ag	0.5	1.5	2.2	2.9	1.2	4.9	1.6	11	24	3.6	╪	╪	2	0.07	0.1	0.05	36
As	1	1	1	2	╪	2	╪	2	7	+	9	6	23	1.8	10	7.2	+
Au(μg/kg)	1	20	10	6	3	6	10	10	9	9	1	2	§	3	3	§	3
B	10	╪	31	15	╪	21	╪	31	╪	+	51	63	16	10	100	33	+
Ba	10	50	22	44	37	54	19	140	150	52	640	820	350	500	600	580	0.1
Be	1	1	1	1	2	2	1	1	╪	+	3	3	2.6	3	3	0.92	+
Bi	3	╪	╪	╪	╪	╪	╪	╪	╪	+	╪	╪	§	0.15	0.2	§	+
Br	1	2	2	2	2	2	1	2	2	2	6	7	§	2.5	5	0.85	0.4
Cd	1	10	20	30	9	20	10	20	40	20	╪	╪	18	0.15	0.3	0.35	60
Cs	1	╪	╪	╪	╪	╪	╪	╪	╪	+	1	2	§	3	7	4	+
Cl	100	╪	160	250	╪	╪	╪	╪	╪	+	╪	330	§	130	170	100	+
Co	1	1	╪	╪	╪	1	╪	1	1	+	6	9	7	22	20	9.1	+
Cr	10	╪	╪	╪	╪	29	╪	71	160	+	540	280	125	100	100	54	+
Cu	0.5	15.8	31.1	41.7	10.2	38.0	14.8	41.7	108	27.6	11.4	16.9	75	50	50	25	0.6
Ge	10	╪	╪	╪	╪	╪	╪	╪	╪	+	╪	╪	§	1.5	1.5	1.2	+
Hf	1	4	1	╪	1	╪	1	1	1	+	2	5	§	3	4	§	+
In	1	╪	╪	╪	╪	╪	╪	╪	╪	+	╪	╪	§	0.06	0.06	§	+
Li	10	╪	╪	╪	╪	╪	╪	╪	╪	+	15	32	5	20	60	24	+
Mn	2	╪	5	10	╪	4	2	4	8	+	400	300	1230	1000	850	550	+
Mo	1	╪	╪	╪	╪	2	1	2	7	+	30	20	9	1.5	2	0.97	+
Nb	10	╪	╪	18	13	╪	13	╪	╪	+	╪	12	§	20	15	11	+
Ni	1	8	10	10	3	7	4	20	40	9	30	40	53	75	80	19	0.1
Pb	2	3	3	6	6	7	6	5	9	5	2	4	50	12.5	20	19	0.3
Pd(μg/kg)	1	4	8	20	4	6	3	9	20	8	3	4	§	§	§	§	+
Pt(μg/kg)	10	╪	╪	╪	╪	╪	╪	╪	10	+	╪	╪	§	§	§	§	+
Rb	10	╪	12	11	25	17	╪	╪	12	+	54	47	§	90	140	67	+
Sb	0.2	0.4	0.3	0.4	0.3	0.7	0.3	0.8	2.9	0.5	1.5	0.6	§	0.2	1.5	0.66	0.3
Sc	0.5	╪	╪	╪	╪	╪	╪	0.7	0.9	+	3.2	5.9	11	20	15	8.9	+
Se	3	4	5	10	4	20	5	70	100	20	╪	╪	4.6	0.05	0.6	0.39	30
Sn	10	╪	╪	╪	╪	╪	╪	╪	╪	+	╪	╪	3	2.5	6	1.3	+
Sr	10	653	613	626	625	674	649	614	681	636	184	316	750	375	400	240	2
Ta	1	╪	╪	╪	╪	╪	╪	╪	╪	+	╪	╪	§	2	2	§	+
Tl	2	╪	╪	╪	╪	╪	╪	╪	╪	+	╪	╪	§	0.8	1	§	+
Th	1	1	╪	╪	╪	╪	╪	╪	1	+	3	6	6.5	8.5	12	9.4	+
W	3	╪	╪	╪	╪	╪	╪	╪	╪	+	╪	╪	§	1.2	1.8	§	+
U	0.5	9.5	8.8	13	5.5	10	11	7.7	12	9.4	0.9	1.5	120	2.7	3.5	2.7	2.7
V	10	19	21	23	14	33	22	43	84	25	31	68	100	110	130	80	0.19
Zn	0.5	27.2	69.5	86.8	18.1	87.4	19.3	112	239	60.0	25.2	45.5	195	70	90	60	0.7
Zr	10	110	30	╪	15	╪	25	28	29	+	65	152	70	165	180	230	+

^{z} denotes detection limit; ^{y} denotes mean of 7 bulk phosphogypsum samples; ^{x} phosphate rock taken from Altschuler (1980); ^{w} taken from Krauskopf (1979); ^{v} taken from Sposito (1989); ^{u} EF = mean phosphogypsum content/shale content; ╪ denotes content below detection limit; + denotes incomplete data set; § denotes data unavailable.

Table 6. Total content (mg/kg) of some rare earth elements (REE) and Y in phosphogypsum and soil samples and literature values for terrestrial material.

Element (Z)[z]	DL[y]	Phosphogypsum Sample # 1	2	3	4	5	6	7	8	Mean[x]	Soil Sand	Till	PR[w]	Crust[v]	Shale[v]	Soil[u]	EF[t]
Y(39)	10	120	120	110	110	120	110	120	120	120	‡	20	275	35	40	25	3
La(57)	0.5	89.9	78.4	80.3	84.7	76.9	85.1	69.1	71.8	80.6	14.4	23	133	35	40	37	2
Ce(58)	3	45	34	35	37	33	35	31	32	36	27	45	104	70	70	48.5	0.5
Nd(60)	5	46	36	32	37	36	32	30	38	36	10	16	98	30	30	46	1
Sm(62)	0.1	6.3	5.2	5.5	5.6	5.1	5.6	4.7	4.9	5.4	1.8	3.0	20	7	7	6.1	0.8
Eu(63)	0.2	1.4	1.4	1.3	1.2	1.1	1.1	1.2	1.3	1.2	0.6	0.8	6.5	1.2	1.4	1.9	0.89
Tb(65)	0.5	1.2	1.0	1.0	1.0	1.0	1.0	0.8	0.8	1	‡	‡	3.2	1	1	0.63	1
Yb(70)	0.2	3.5	2.7	2.8	2.7	2.7	2.8	2.6	3.0	2.8	0.9	1.5	12.6	3.5	3.5	2.3	0.81
Lu(71)	0.05	0.51	0.36	0.44	0.38	0.39	0.44	0.36	0.45	0.41	0.13	0.22	2.7	0.6	0.6	0.34	0.7
SumREE		190	160	160	170	160	160	140	150	160	55	90	380	150	150	140	1.1
SumLa[s] / SumLu[r]		36	38	36	41	37	37	36	35	37	52	51	20	28	29	43	1.3

[z] denotes atomic number; [y] denotes detection limit; [x] denotes mean of 7 bulk phosphogypsum samples; [w] taken from Altschuler (1980); [v] taken from Krauskopf (1979); [u] taken from Sposito (1989); [t] EF = mean phosphogypsum content/shale content; [s] denotes elements from La to Eu; [r] denotes elements from Tb to Lu; ‡ denotes content below detection limit.

The level of CaO in the phosphogypsum samples corresponds closely to the level expected in pure gypsum ($CaSO_4{*}2H_2O$) of 32.6%. The slightly lower levels in the phosphogypsum can be attributed mainly to dilution by residual noncrystal water in the air dried samples and to impurities present in the material which are dominated by SiO_2. These results correspond closely to the assessment of the material using x-ray diffraction which confirmed that it is generally over 90% gypsum with no mineral impurities being detectable except quartz. However, SO_3 levels were in excess of the 46.5% expected in pure gypsum by up to 1.48 times suggesting that there was some inaccuracy in the x-ray fluorescence technique used for this element.

2. Trace Elements

As in an earlier study by Roberts Thorne (1990) on the same phosphogypsum stack, the following trace elements were found to be significantly enriched relative to shale: Ag, Cd, and Se, with samples ranging from at or near 10 times enriched to as high as 240 times in the case of sample 8 with Ag (Table 5). Gold, Sr and U showed only slight enrichment (at least 2 times). Those elements significantly depleted were Co(20x) and Mn(150x) in samples with detectable levels. Arsenic, B, Ba, Be, Br, Cs, Hf, Li, Ni, Pb, Rb, Sb, Sc, Ta, Th, V, and Zr were slightly depleted while the remainder of the trace elements present in samples with detectable levels occurred at comparable levels to those found in shale.

Samples 7 and particularly 8 had somewhat elevated levels of Ag, As, Ba, Cd, Cr, Cu, Mo, Ni, Sb, Se, V, and Zn relative to the other samples. These samples were blacker, especially sample 8, and richer in organic C than the other samples suggesting that organic matter may be an important factor involved in the attenuation of at least a portion of the trace elements listed above. The list above corresponds closely to the same list for phosphate rock (Krauskopf 1955; Gulbrandsen 1966). In phosphate rock this correlation of elemental levels with organic matter content has been attributed to either organic complexing or to the presence of metallic sulfides produced under anaerobic conditions stimulated by an excess of organic accumulation over available oxygen.

3. Rare Earth Elements

The elements from atomic numbers 57 to 71 are the rare earth elements (REE) and are members of Group IIIA in the periodic table. The group has been subdivided into two groups; the light REE which range from La to Sm and the heavy REE ranging from Gd to Lu. Yttrium (atomic number 39) is frequently discussed with members of the REE as it has similar chemistry and is also a member of the Group IIIA (Henderson 1984). All of the REE have similar chemical and physical properties related to the nature of their electronic configuration leading to a relatively stable 3^+ oxidation state and a gradual increase in ionic radius with increase in atomic number for a given co-ordination number. However, this group of elements can be partially fractionated by a number of natural processes and this characteristic has been used to study mineral genesis, and weathering. Little is known about the impacts of the REE on the environment and so it is important to document their content in phosphogypsum so that this information is available should any of the REE become of environmental concern.

Seven REE plus Y were measured (Table 6). Of the REE only La showed much enrichment relative to shale and crustal materials. Yttrium(3x) was enriched to a greater degree than La(2x) relative to shale. Neodymium was enriched by less than 2x, while none of the heavy REE were elevated relative to shale. The total sum of the REE measured in phosphogypsum was comparable to that of shale. Within phosphogypsum, the REE and Y relative distribution followed closely the distribution found in phosphorites although phosphate rock has a greater overall sum of REE. Although Ce is dominant in many apatites (Fleischer and Altschuler 1969), those of marine sedimentary origin tend to be dominated by La or Nd. This has been attributed to the depletion of Ce in sea water by oxidation of Ce^{+3} to Ce^{+4} and its removal through precipitation in hydrous Mn oxides. There is very little difference among phosphogypsum samples in the content of specific REE and Y supporting the theory that substitution within the gypsum or fluorapatite structure (Altschuler 1980) or precipitation in a pure phase is the dominant form of these elements rather than organic complexing or a related process.

The ratios of light REE to heavy REE ranged from 36 to 41 for the phosphogypsum samples which was comparable with the standard soil values (Table 6). The phosphate rock, crust and shale ratios were somewhat lower and the sand and till somewhat higher. In the case of the soil samples, the enrichment of light REE indicated by a high light REE to heavy REE ratio in soils relative to shale or crustal materials has been attributed to chemical weathering particularly in hot humid environments (Balashov *et al.* 1964) and to a greater stability of aqueous inorganic and organic complexes with heavy REE than with light REE (Ronov *et al.* 1967; Varshal *et al.* 1975). During the dihydrate process, the tendency for heavy REE to more readily move into solution through complex formation relative to light REE may be important in determining the high ratio of light REE to heavy REE found in phosphogypsum relative to phosphate rock.

C. Radioactivity

Data collected on the relative level of radionuclides present in the samples were not absolute as no standard was prepared in our laboratory. From the analysis in the absence of a standard it was possible to compare samples for relative amounts of ^{226}Ra using peak areas per gram established in the literature for the decay series of interest. The ^{226}Ra daughter product peaks which have been used in ^{226}Ra quantification are the 295 and 352 KeV peaks of ^{214}Pb and the 609 KeV peak of ^{214}Bi (Bolch *et al.* 1977). The sum of the peak areas per gram of these three ^{226}Ra decay products is directly related to ^{226}Ra levels. Samples of material from the Medicine Hat stack contain on average 0.5 Bq g^{-1} Ra (Roberts Thorne 1990) and from this study an average of 9.4 mg kg^{-1} U, and up to 1 mg kg^{-1} Th.

Sample 7 had the highest number of counts per gram over 24 hours (Table 7). This sample fell among the acidic, more buffered group of samples and was enriched in organic C with at least twice as much as any of the other six bulk samples. Samples 1 and 6 were from the less acidic, less buffered, and lower organic C group and were close together at the low end in levels of ^{226}Ra. From low to high, the rest of the samples fell in the following order on a continuum: 4, 2, 3, and 5.

Subsamples were batch incubated for 6 months at a 1:2 solid:solution ratio, and extracted to remove soluble constituents by pouring five separate aliquots of distilled deionized water over the sample, each followed by filtration under suction using a buchner funnel. Compared to samples which were not batch incubated and extracted, samples 2, 4, and 5 showed a net loss of ^{226}Ra (Table 7). However, changes of less than 5% could not be considered significant as the precision of the technique rested at this level. Thus the only samples showing a significant change were 4 and 5. Samples 4 and 5 lost 8 and 6% of the original ^{226}Ra respectively through batch incubation and deionized water extraction.

Based on theoretical considerations, the majority of the samples, which showed no significant change with batch incubation and deionized water extraction, evidenced the most predictable trends as ^{226}Ra is not expected to be readily released from this material (May and Sweeney 1984). It has been estimated that Ra moves at 1/215 times the seepage rate for Ra in a U tailings pond seeping through alluvial soil (United States Nuclear Regulatory Commission 1980 as cited by May and Sweeney 1984).

Table 7. Levels of ^{226}Ra daughter products in phosphogypsum (peak area/g/24 hours).

Sample and Treatment	Isotope (KeV)			
	Pb-214 (295)	Pb-214 (352)	Bi-214 (609)	Sum
1 Control^{z}	130	220	150	500
1 Extracted^{y}	130	220	150	500
Diff(%)^{x}	0	0	0	0
2 Control	170	280	190	640
2 Extracted	170	270	190	630
Diff(%)	0	4	0	1
3 Control	220	360	250	830
3 Extracted	220	360	250	830
Diff(%)	0	0	0	0
4 Control	150	260	170	580
4 Extracted	140	230	160	530
Diff(%)	7	10	6	8
5 Control	260	430	290	980
5 Extracted	250	400	270	920
Diff(%)	4	7	7	6
6 Control	130	220	150	500
6 Extracted	130	220	150	500
Diff(%)	0	0	0	0
7 Control	350	570	390	1300

^{z} stored at 5°C; ^{y} batch incubated and extracted with distilled deionized water; ^{x} difference expressed as a percentage of control.

In the study of Ra geochemistry, it was observed by Langmuir and Riese (1985) that Ra concentrations in ground water were always too low to reach saturation with respect to a pure Ra phase of which $RaSO_4$ would generally be the least soluble. Radium concentrations were thus concluded to be limited in natural waters by adsorption or by solid solution formation or both. Langmuir and Melchoir (1985) found that all deep brine samples collected from Palo Duro Basin of north Texas were undersaturated by 5 to 6 orders of magnitude with respect to pure $RaSO_4$. Levels of ^{226}Ra in the brines ranged from $10^{-11.3}$ to $10^{-12.7}$ mol kg^{-1} and were not controlled by $RaSO_4$ solubility or adsorption but rather more likely by trace solid solutions in sulphates including celestite and barite. Similar solid solutions likely occur in phosphogypsum. Therefore, in this study, an undetectable amount of Ra would be expected to be released through the incubation and extraction procedure followed.

D. Pore Water Chemistry and Computer Modelling

Solution extracts from the batch incubation harvested at 60 and 80 days and from the time trial were analysed for 26 elements by inductively coupled plasma-atomic emission spectroscopy (ICP). Samples from all treatments were frozen prior to elemental analysis. Levels of pH and electrical conductivity (EC) were analysed on all samples both before and after freezing. Subsamples from the 80 day harvest of the batch incubation of the phosphogypsum alone treatment were left unfrozen prior to elemental analysis. An examination of the effects of time, freezing and soil additions on solution chemical parameters has been provided below. Ion activity and ionic strength (IS) levels generated with the use of GEOCHEM, along with some measured chemical parameters have been examined graphically with respect to the effect of time of equilibration. The computer generated IS has been compared with that calculated from EC measurements (IS = 0.013EC) (Griffin and Jurinak 1973). A discussion of the computer generated ion balance and percentage distribution of elements into their species in a select sample was provided.

Drinking water standards were compared with pore water levels in order to identify elevated levels of noxious elements. This information was used as an aid in the selection of elements to be examined using solubility equilibria diagrams in the following section.

1. Time Trial

Time trial data has been presented in graphical form with each figure containing plots of the means of three replicates for each phosphogypsum treatment as well as the gypsum trial where data were available (Fig. 12-31). Tables of the analytical data from all batch incubations have been included in Appendix II. Distributions of the divalent calcium and sulphate activities in the phosphogypsum alone treatment (Fig. 12 and 13) followed comparable trends and were somewhat erratic particularly at the 60 to 90 day sampling period. When converted to an ion activity product and related to a gypsum solubility isoline (Fig. 14) they were near saturation during the initial 14 days and undersaturated at other sampling times. Sample treatments which tended to have a high relative SO_4^{2-} level (e.g. PG1:S1) had a low relative Ca^{2+} level and *vica versa*.

The erratic behavior observed was likely due to sample handling, rather than a time effect. When samples were thawed prior to analysis a small amount of gypsum precipitate, which formed during freezing, persisted. The observed undersaturation and erratic fluctuations can be explained by the freezing effect. It was not possible to consistently control the freezing-induced precipitation among sampling dates. The apparent equilibrium relative to gypsum solubility at 7 days or less was consistent with the 10-day equilibration time adopted in earlier gypsum solubility studies (Rance and Davey 1968; Bennett and Adams 1972).

Little to no precipitate was observed in the PG10:S1 and PG1:S1 treatments. Both the Ca^{2+} activities and particularly the SO_4^{2-} activities demonstrated more stable behaviour in these cases. These samples were undersaturated with respect to gypsum indicating that calcium carbonate and/or calcium adsorption may have been affecting Ca^{2+} activity. Generally gypsum can exist in a soil environment when the sulphate activity approaches 10^{-2} mol L^{-1} (Lindsay 1979). However, calcium carbonate starts to dominate calcium activity at pH > 8.0. Between pH 7.5 and 8.0, gypsum and calcite can coexist. This was likely what occurred in the PG1:S1 treatment where the pH ranged from 7.4 to 7.6. In the PG10:S1 treatment where the pH ranged from 6.2 to 6.9, it may have been occurring combined with the freezing effect. The full conversion from calcite to gypsum or from gypsum to calcite as governed by thermodynamics was also restricted by the physical constraint of crystal surface area which limited the amount of surface available to react.

An equilibration time seemed to be required for pH particularly in the PG1:S0 and the PG10:S1 treatments (Fig. 15). The initial pH measured after one day incubation decreased slightly over 7 days by approximately 1 pH unit for the PG1:S0

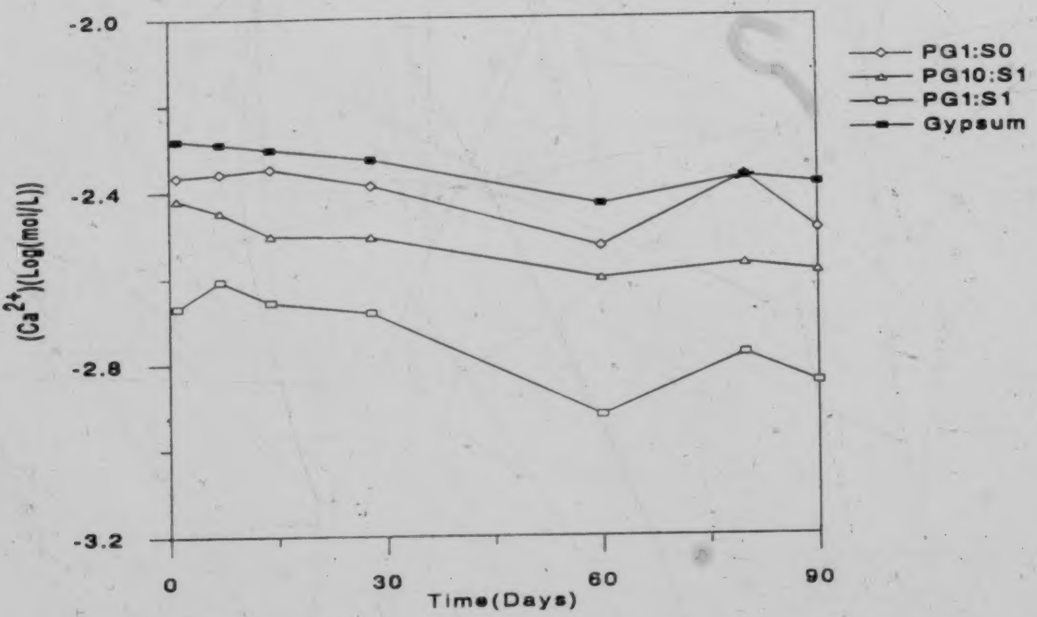

Figure 12. Activity of Ca^{2+} over time.

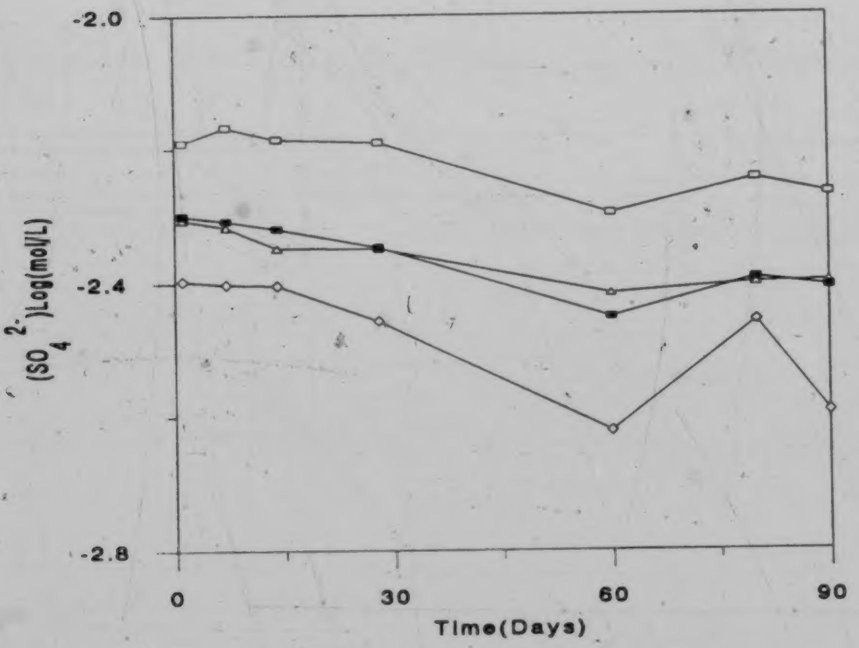

Figure 13. Activity of SO_4^{2-} over time.

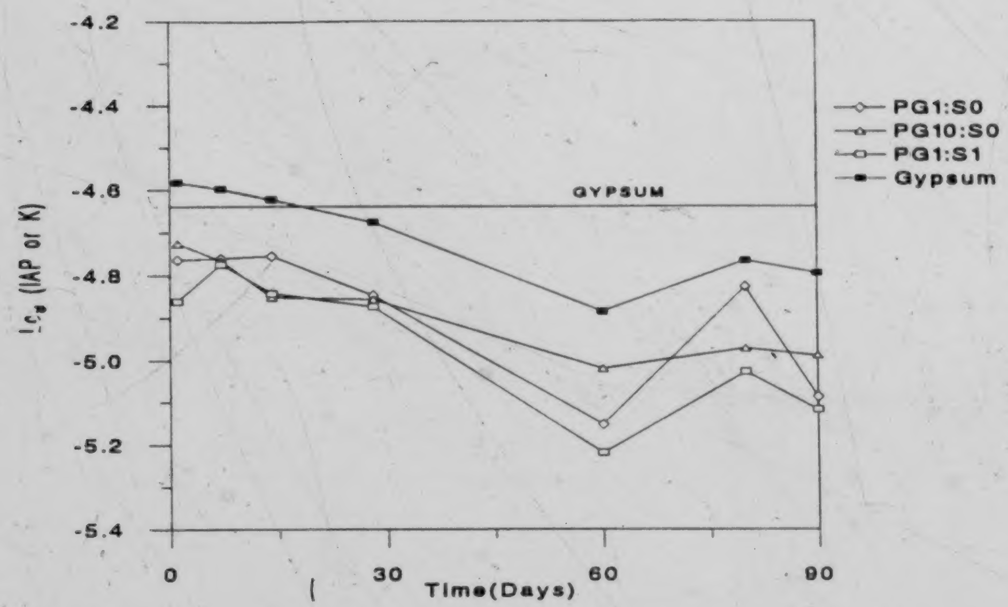

Figure 14. Gypsum equilibrium and ion activity product (IAP) over time. Thermodynamic data from Lindsay (1979).

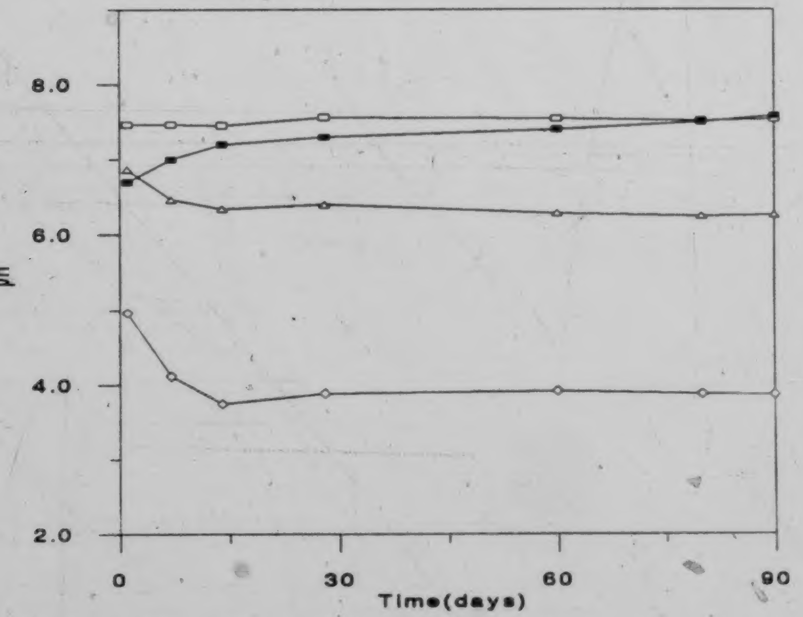

Figure 15. Change in pH over time.

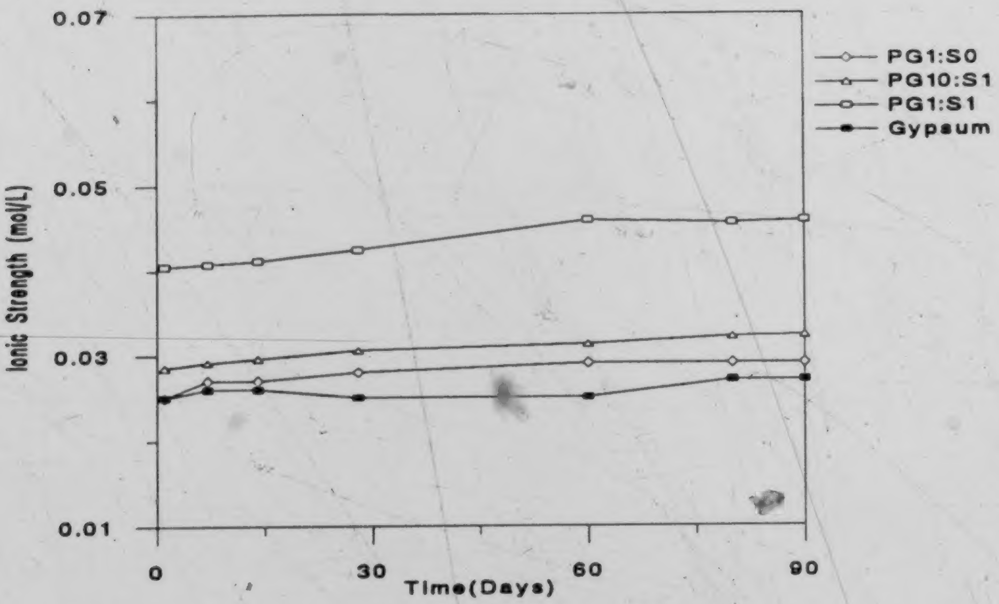

Figure 16. Ionic strength (calculated from electrical conductivity) over time.

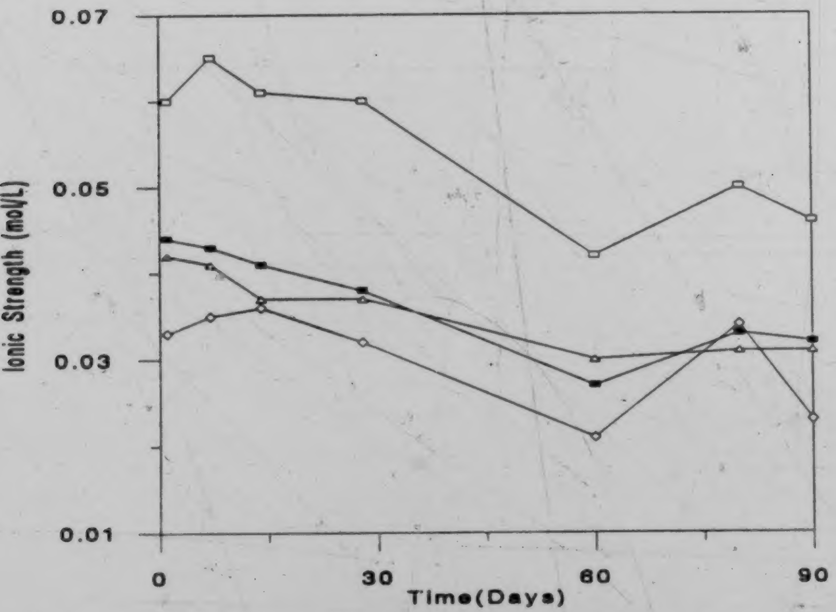

Figure 17. Ionic strength (calculated using GEOCHEM) over time.

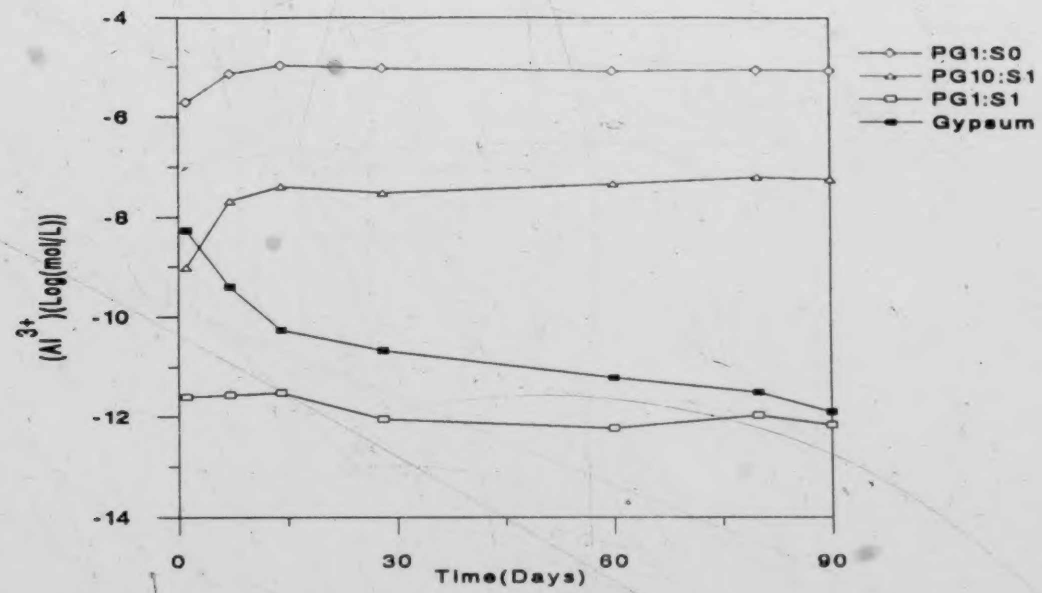

Figure 18. Activity of Al^{3+} over time.

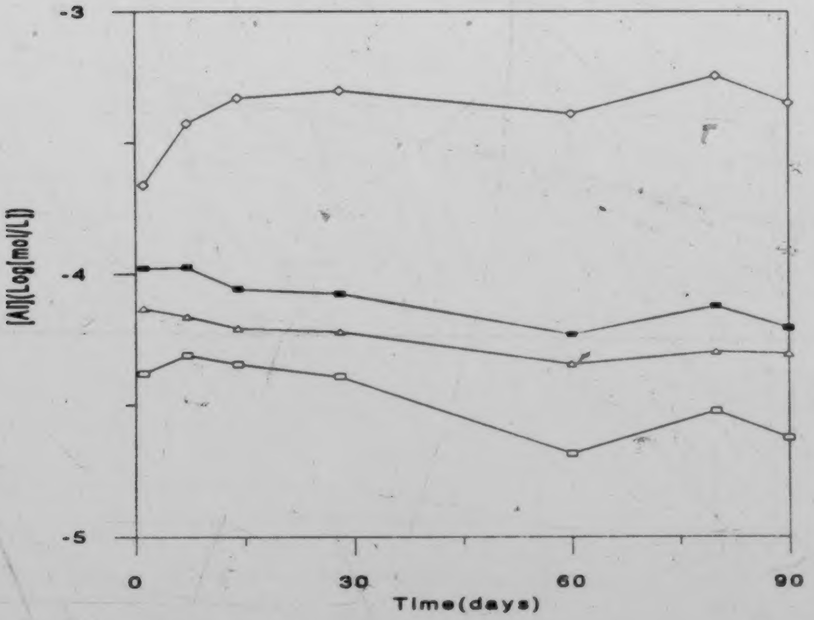

Figure 19. Concentration of Al over time.

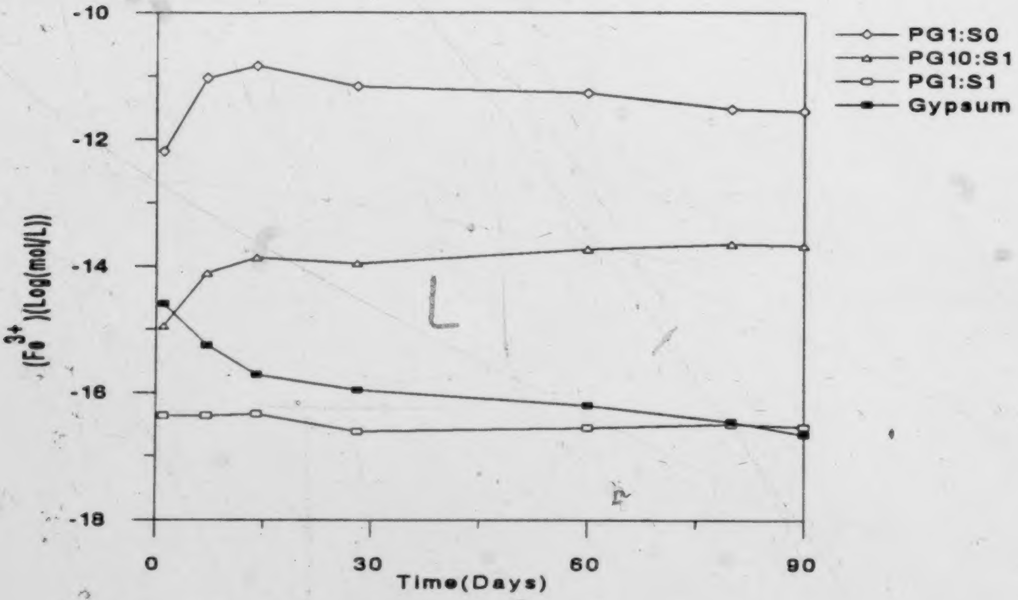

Figure 20. Activity of Fe^{3+} over time.

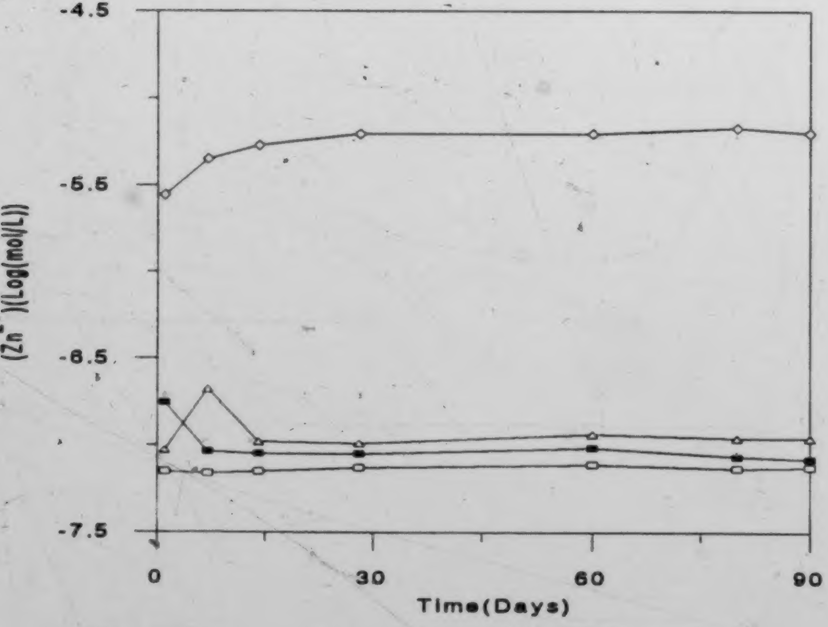

Figure 21. Activity of Zn^{2+} over time.

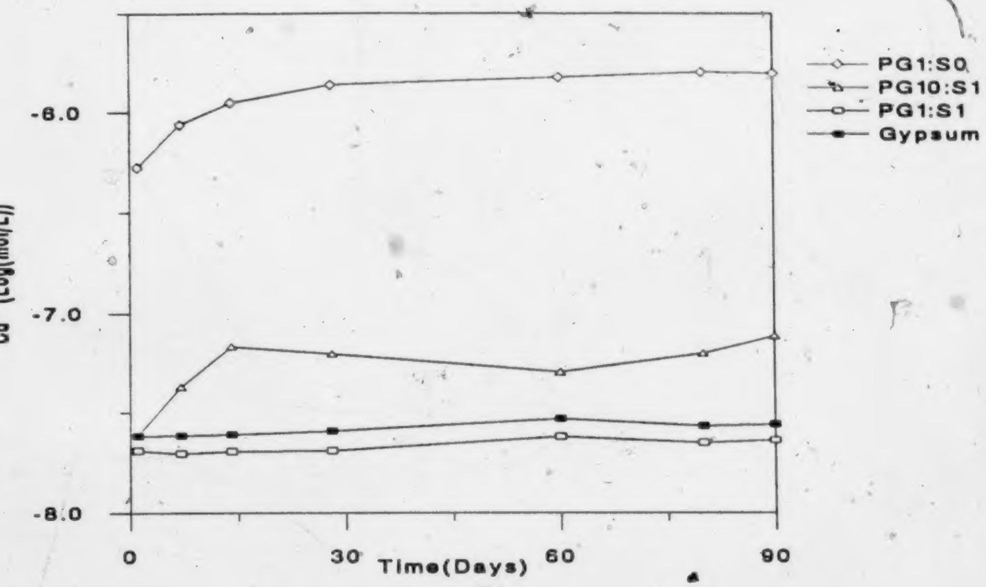

Figure 22. Activity of Cd^{2+} over time.

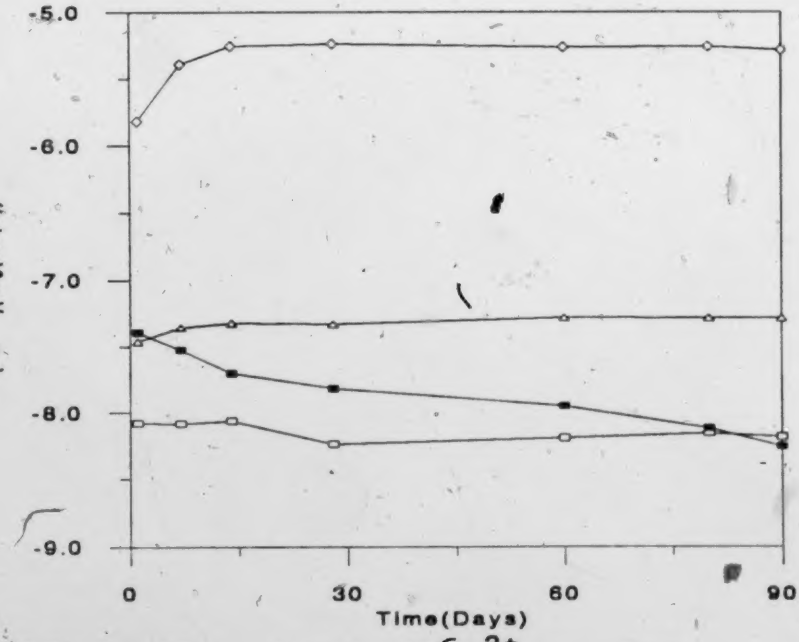

Figure 23. Activity of Cu^{2+} over time.

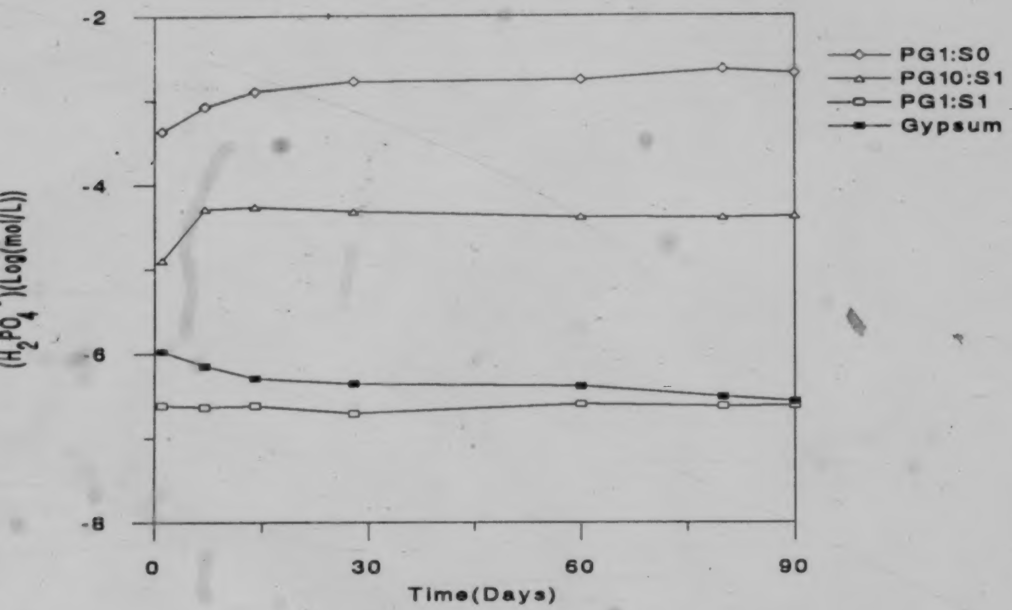

Figure 24. Activity of $H_2PO_4^-$ over time.

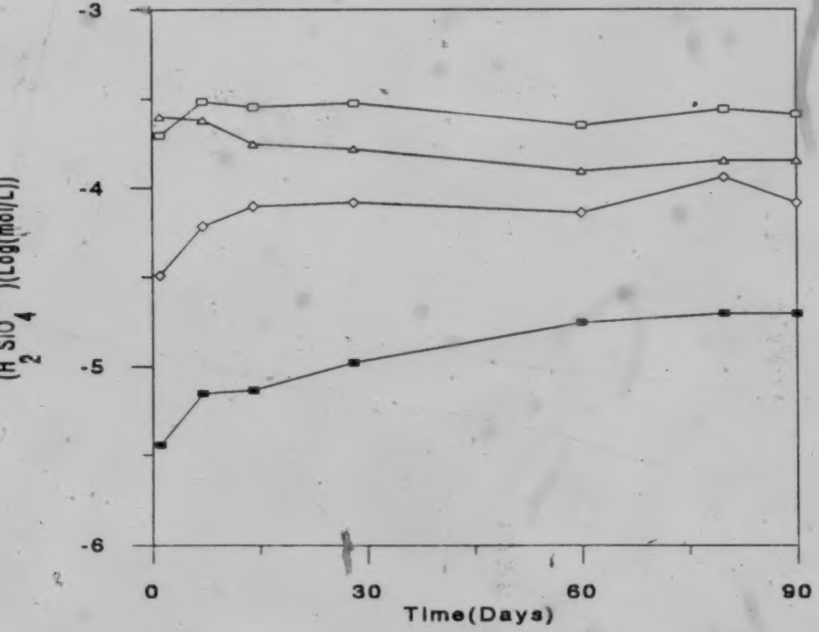

Figure 25. Activity of $H_2SiO_4^{2-}$ over time.

treatment and by approximately 0.4 pH units in the PG10:S1 treatment. The pH decreased up to 0.3 units more by 14 days in these two treatments and stabilised at or near this level over the remaining incubation period. For the PG1:S1 treatment, the pH was nearly constant as it only oscillated slightly during the time period over approximately 0.2 pH units. The initial increase in acidity in the PG1:S0 and the PG10:S1 samples was likely due to several factors including the gradual break down of the less than 0.2-mm phosphogypsum crystals and crystal aggregates through agitation and dissolution and the release of entrapped inner aggregate surface hydrogen and phosphoric acid molecules and fluid inclusions within gypsum crystals, and the gradual diffusion outward of hydrogen and phosphoric acid molecules from micropores.

A number of the ion activities monitored appeared to follow an inverse trend relative to pH (Fig. 18, and 20-25). This pH effect was attributed to the inverse relationship between many mineral solubilities and pH. However, adsorption reactions involving a number of the cations of interest have also been observed to have this type of pH dependency (Cavallero and McBride 1978; Puls and Bohn 1988).

Since Ca^{2+} and SO_4^{2-} activities, two of the major solution species, did not follow an inverse pH trend, ionic strength (IS) generally did not follow this trend. Ionic strength seemed follow the erratic fluctuations observed in Ca^{2+} and SO_4^{2-} activities (Fig. 16 and 17). Ionic strength was determined two ways, IS calculated from EC measured in unfrozen samples (IS = 0.013EC) (IS(U)) (Griffin and Jurinak 1979), and IS calculated by GEOCHEM derived from measured elemental concentrations (ISmod). For all treatments of ISmod, the erratic fluctuations of the Ca^{2+} and SO_4^{2-} activities were followed closely. The PG1:S0 and PG10:S1 treatments from IS(U) demonstrated a slightly inverse trend relative to pH which was likely due to an increase in the concentration of species other than Ca^{2+} and SO_4^{2-}, particularly PO_4^{3-}, and its complexes with an increase in acidity.

In all treatments, the IS varied between 0.02 and 0.07 M. Modelled ionic strength values were greater than IS(U) values at most sampling dates. This may be due to limitations of the empirical equation. The ISmod values were more variable than those calculated from EC which was attributed to the numerous sources of variation incorporated into the ISmod calculated result including that F and Cl concentrations were not accounted for nor were variations in their levels among samples; and the fluctuations in each ion activity over time were incorporated into the ISmod.

The activities of Al^{3+}, Cd^{2+}, Cu^{2+}, Fe^{3+}, $H_2PO_4^-$, $H_2SiO_4^{2-}$ and Zn^{2+} all varied inversely with pH (Fig. 18, and 20-25). Most of the elements of the ions listed above were at or near the detection limit in the PG1:S1 treatments. In this treatment, they did not fluctuate a great deal which was attributed to their near detection limit levels as well as to a low variation in pH.

Some of the apparent pH dependent behavior was related to solution speciation since at higher pH values a greater proportion of the metal was complexed by hydroxyl ions and other ligands than at lower pH levels where a greater proportion of the cation was free; this being true for Al^{3+}, Cd^{2+}, Cu^{2+}, and Zn^{2+} (Table 11). Most of the aqueous Fe was continuously complexed while the proportion of phosphate complexed with hydrogen increased as pH increased. However, in the equilibrated systems the pH effect was likely primarily attributable to solubility reactions. This was supported by observed unspeciated concentration over time distributions which showed apparent inverse pH trends in the PG1:S0 treatment for the elements listed above. As an example, a time distribution for Al concentration has been included (Fig. 19). There are notable erratic fluctuations in the 60 to 90 day period due to the direct effects of fluctuating ionic strength, and these effects are eliminated through ion activity calculations. The erratic fluctuations observed in the Ca^{2+} and SO_4^{2-} activities were also evidenced in the distribution of $H_2SiO_4^{2-}$ activities particularly in the PG1:S0 treatment (Fig. 25).

A mined gypsum sample alone was also included in the time trial study. Its pH was close to that of the PG1:S1 treatment. It demonstrated the freezing effect showing the same erratic fluctuations in Ca^{2+} and SO_4^{2-} activities evidenced in the PG1:S0 treatment but to a lesser degree (Fig. 12 and 13). Uniquely, there was a slight increase in pH during the first two weeks of incubation (Fig. 15) and the activity of ions such as Al^{3+}, Cu^{2+}, Fe^{3+}, $H_2PO_4^-$, and Zn^{2+} (Fig. 18, 20, 21, 23 and 24) all followed an apparent inverse trend relative to pH; their activities decreased rather than increased initially. Activities stabilised near those of the PG1:S1 treatment in most cases. The pH trend observed was likely due to agitation and dissolution leading to the release of OH^- over time, which produced an increase in pH by over one pH unit. The solution contents of the mined gypsum were higher than those of the PG1:S1 mixes in some cases such as Al concentration (Fig. 19). Part of the cause of higher values may be due to a freezing induced precipitate present in the mined gypsum which did not completely settle and thus interfered with the solution analysis. This was a unique problem for the gypsum samples due to a lower amount of total solution available.

Time effects on activities of some As, Cr and Se species were also examined (Fig. 26-31) as the solubility controlling solids for these species are discussed in a later section. The $HAsO_4^{2-}$ activity was stable for all treatments except PG1:S0 in which it

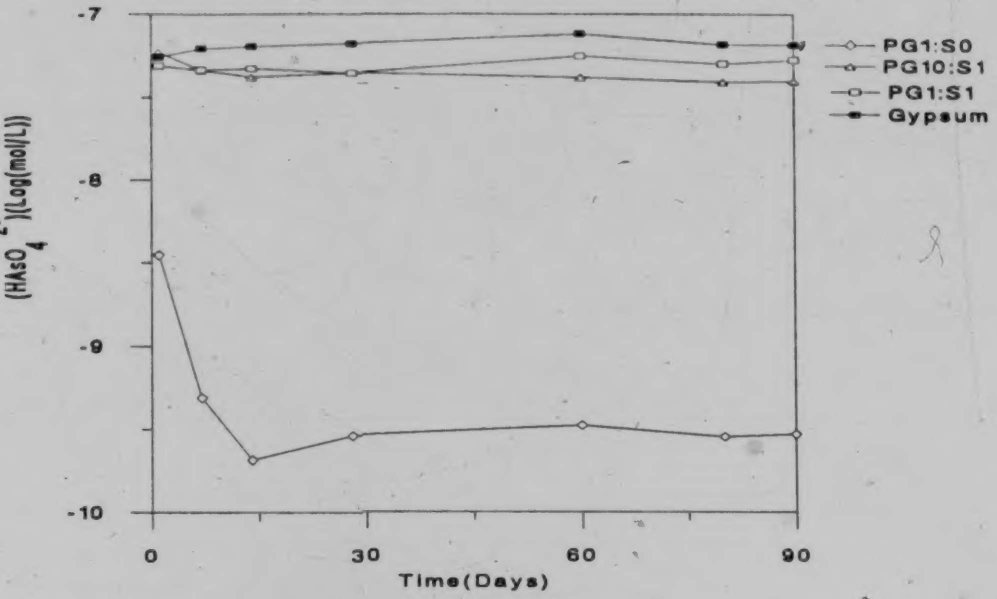

Figure 26. Acitivity of $HAsO_4^{2-}$ over time.

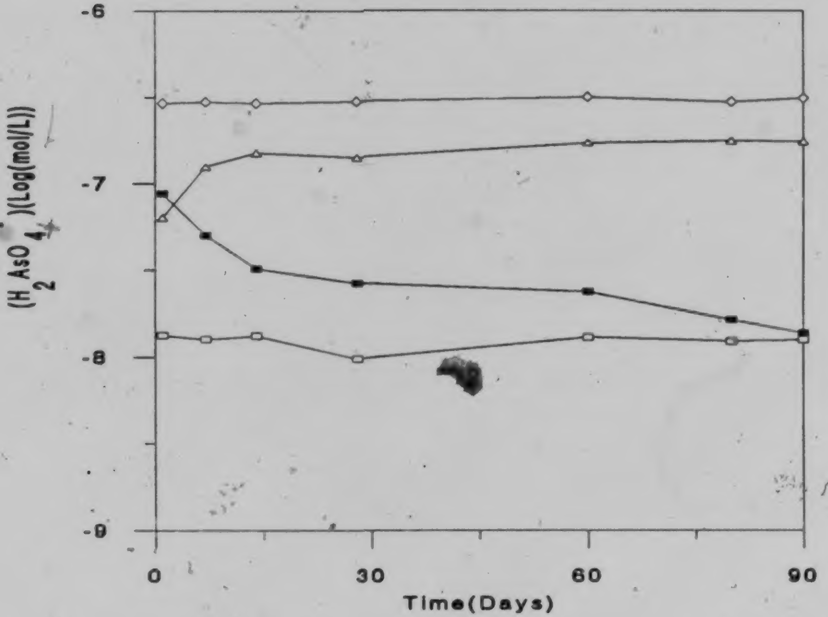

Figure 27. Activity of $H_2AsO_4^-$ over time.

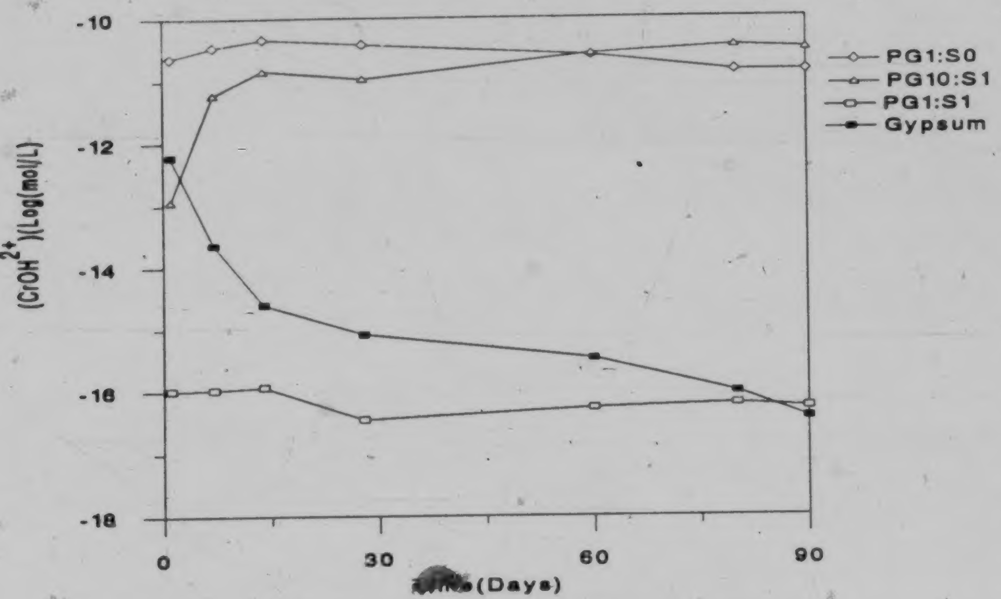

Figure 28. Activity of CrOH $^{2+}$ over time.

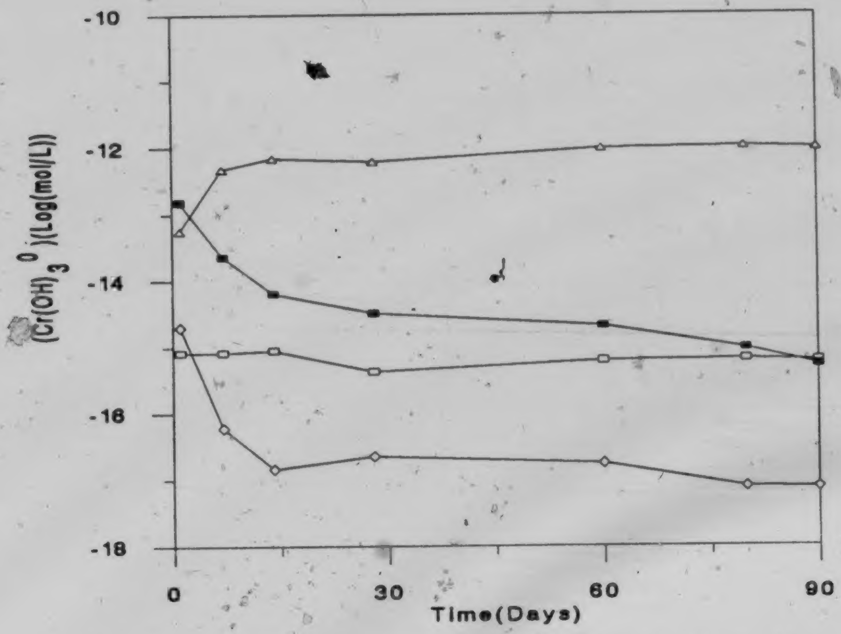

Figure 29. Acitivity of Cr(OH)$_3$^{0} over time.

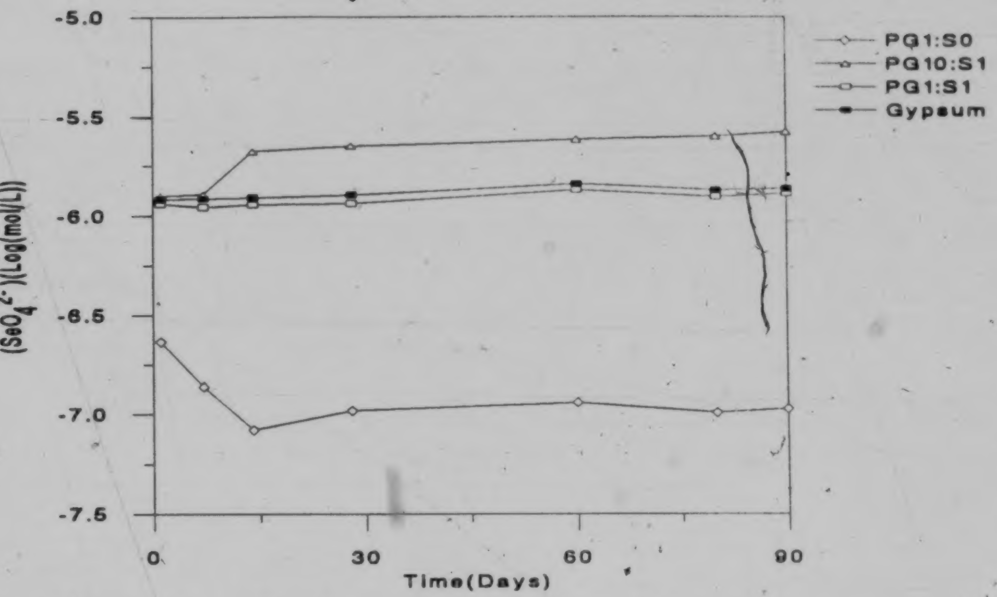

Figure 30. Activity of SeO_4^{2-} over time.

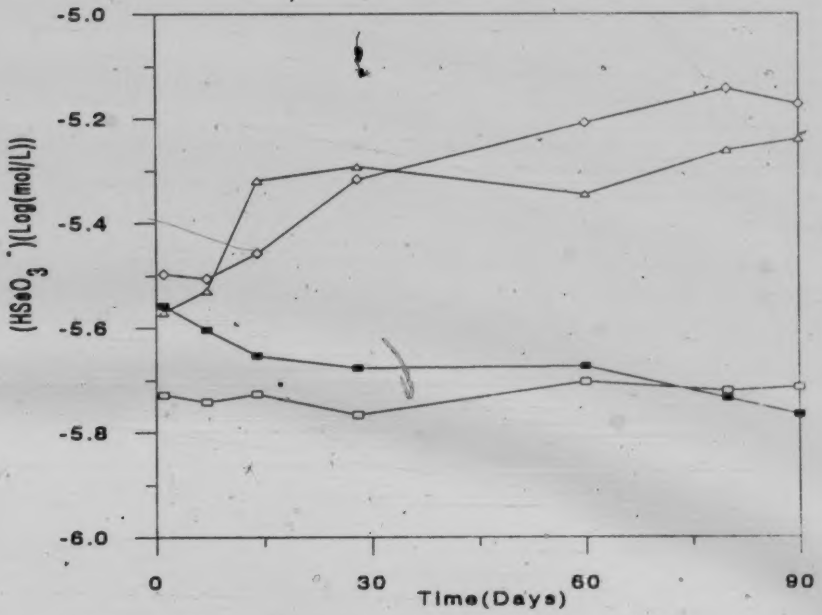

Figure 31. Activity of $HSeO_3^-$ over time.

was several orders of magnitude lower and showed a direct relationship with pH (Fig. 26). The activity of $H_2AsO_4^{1-}$ showed an apparent inverse response to pH for the PG10:S1 and Gypsum treatments (Fig. 27). The PG1:S0 and PG1:S1 treatments had constant $H_2AsO_4^{2-}$ activity levels over time. These responses were entirely due to speciation since the entered As concentration was stable at the detection limit.

Generally $Cr(OH)^{2+}$ activity increased initially only slightly in the PG1:S0 and by nearly 2 orders of magnitude in the PG10:S1 treatment, but in the Gypsum treatment it decreased abruptly by 3 orders of magnitude during the first 30 days of incubation and then levelled off, decreasing slightly after 60 days (Fig. 28). The trends observed in the PG10:S1 and the PG1:S1 were entirely due to speciation effects as the concentration of Cr did not change appreciably and it was at or near the detection limit. The $Cr(OH)_3^0$ activity levelled off for all treatments after about 14 days showing an initial decrease in the PG1:S0 treatment and an apparent inverse relationship with pH in the PG10:S1 and Gypsum treatments (Fig. 29). The PG1:S0 treatment generally had the highest activity of $Cr(OH)^{2+}$ and the PG10:S1 treatment had the highest activity of $Cr(OH)_3^0$.

The activity of SeO_4^{2-} decreased initially in the PG1:S0 treatment and activity levels were relatively low (Fig. 30). The activity of $HSeO_3^-$ increased slightly in the PG1:S0 and the PG10:S1 treatments and decreased in the Gypsum treatment (Fig. 31). Both of these effects were attributed to the effects of speciation on ion activity. Other treatments showed no obvious trends for the two Se species but activities were quite stable over time. Selenium ion activities are not expected to be controlled by dissolution reactions under the oxidising conditions expected in most waste leaching environments (Rai *et al.* 1987a). If a rapid equilibrium solubility reaction was occurring, it could make up for any speciation effects (i.e. Al total concentration was apparently related to pH regardless of speciation effects)(Fig. 19).

2. Effects of Time, Treatment and Soil Additions on Pore Water Chemistry

Simple paired T tests pairing the means of a set of 3 replicates of the same treatment and sample were performed to further examine any changes with time on solution parameters. Solution chemical parameters of the 60 and 80 day batch incubation harvests were compared as were frozen and unfrozen samples for the PG1:S0 pore water extracted at 80 days.

Of the PG10:S1 and PG1:S1 treatments, none of the parameters were significantly different except electrical conductivity from previously frozen samples

(EC(F)) for both and Si in the PG10:S1 treatment (Table 8). For PG1:S0 a number of elements varied significantly for the two harvest times including Al, Ca, Cd, Mg, Ni, Se, and Sr. It is expected that at least part of these differences was attributable to uneven freezing and thawing. Some of the differences may disappear through speciation when the effects of varied ionic strength are taken into account as illustrated for Al in the time trial (Fig. 18 and 19). Elements present at very low levels, including Ni, Cd and Se, need only fluctuate by a small absolute amount to be significant. Solid to solution ratio may have varied slightly between the 60 and 80 day harvest as the slurry aliquot removed may have been slightly different in solid to solution ratio than the bulk slurry. Changes in solid to solution ratio can affect adsorption (McBride 1989). Desorption of Co^{2+} and Ni^{2+} from montorillonite has been observed upon concentrating the clay, an indication that the adsorption affinity of the metal is reduced by increasing the solids concentration (DiToro *et al.* 1986).

Solution parameters which showed a significant effect of freezing evidenced using a paired T test for comparison were Al, Ca, Fe, P, S, Se, Si, Sr, and Ti (Table 8). Most of these elements were expected to readily form either pure or substituted minerals in the system and thus it is not surprising that with the induction of crystallization of gypsum through freezing there was also the establishment of accessory minerals such as amorphous silica or fluorapatite. The primary elements associated with well-established mineral phases are covered in more detail in the following section.

Measurements for pH and electrical conductivity (EC) for all samples before and after freezing were also compared (Table 9). The pH level varied significantly in the PG1:S0 incubated for 60 days (PG1:S0(60)), PG10:S1(60) and PG10:S1(80) treatments. Generally through freezing, the pH decreased. Samples 1, 4 and 6 showed the greatest degree of variation with freezing decreasing from a pH level near 6 to one near 5. These samples all were less buffered than the other four. It is likely that the carbonate reactions were starting to dominate the pH in this system and that with freezing and thawing in a bottle sealed to the atmosphere, a change, likely a decrease in the solution carbonate occurred thereby leading to a lowering of the pH. In those systems with more added carbonate (PG1:S1) the pH was more stable with freezing and it did not change significantly through freezing.

Electrical conductivity varied significantly before and after freezing in all of the treatments except PG10:S1(60) (Table 9). At least two factors were likely involved, the precipitation of gypsum and/or calcium carbonate and other trace minerals and solid solutions through freezing, and the reaction of CO_2 through freezing and thawing in a sealed container.

Table 8. Effects of time and treatment on pore water chemistry.

	60 day vs. 80 day			F vs U (80)
Parameter	PG1:S0	PG10:S1	PG1:S1	PG1:S0
Al	*	NS	NS	*
As	+	+	+	+
B	+	+	+	+
Ba	+	+	+	+
Ca	*	NS	NS	*
Cd	*	+	+	NS
Co	+	+	+	+
Cr	+	+	+	+
Cu	NS	+	+	NS
Fe	NS	+	+	*
K	NS	NS	+	NS
Li	+	+	+	+
Mg	*	NS	NS	NS
Mn	NS	NS	+	NS
Mo	+	+	+	+
NH_4^+-N	NS	NS	NS	+
NO_3^--N	NS	NS	NS	+
Na	NS	NS	NS	NS
Ni	*	+	+	NS
P	NS	NS	+	*
Pb	+	+	+	+
S	NS	NS	NS	*
Se	*	+	+	*
Si	NS	*	NS	*
Sr	*	NS	NS	*
Ti	NS	+	+	*
V	NS	+	+	NS
Zn	NS	+	+	NS
pH(U^z)	NS	NS	NS	NS
pH(F^y)	NS	NS	NS	NS
EC^x(U)	NS	NS	NS	NS
EC(F)	NS	*	*	*

* denotes statistically significant difference at $P=0.05$; NS denotes $P>0.05$; + denotes incomplete data set; ^{z} denotes samples left unfrozen prior to analysis; ^{y} denotes samples frozen prior to analysis; ^{x} electrical conductivity.

Table 9. Effects of treatment and analytical technique on pore water chemistry.

	F[z] vs U[y]		Modelled vs. Calculated	
Treatment	pH	EC	IS(U)	IS(F)
PG1:S0(60)	*	*	NS	*
PG1:S0(80)	NS	*	*	*
PG1:S0(U80)	╫	╫	NS	╫
PG10:S1(60)	*	NS	*	*
PG10:S1(80)	*	*	NS	*
PG1:S1(60)	NS	*	NS	*
PG1:S1(80)	NS	*	NS	*

[z] denotes samples frozen prior to analysis; [y] denotes samples left unfrozen prior to analysis; * denotes statistically significant difference at $P=0.05$; NS denotes $P>0.05$; ╫ denotes comparison does not apply.

In general the modelled ionic strength (ISmod) was not significantly different from that calculated from electrical conductivity (EC) measurements from unfrozen extracts (IS(U)). Only samples PG1:S0(80) and PG1:S10(60) were significantly different in this respect. The frozen EC generated a calculated IS (IS(F)) which was in all cases significantly different and lower than the ISmod. The empirical equation relating EC to IS may not be appropriate for these systems.

3. Ion Difference and Distribution of Species

The ion difference calculated using GEOCHEM for all of the batch incubated sample treatments ranged from 3.4 to 34% of total cationic charge (Table 10). Mean values calculated for the different treatments ranged from 7.1 to 21%. In all cases there was an excess of cations which could be partly explained by the lack of measured Cl and F for input data. Fluoride is a particularly important anion in phosphogypsum systems (Murray and Lewis 1985). For Florida phosphogypsum the level of F is approximately 6800 mg kg^{-1} and Cl is 61 mg kg^{-1} (May and Sweeney 1980).

In general the more buffered, more acidic samples (samples 2, 3, 4, and 7), particularly when previously frozen, had greater ion differences than the less acidic, less buffered samples (samples 1, 4, and 6). There was likely more F^- and Cl^- in solution in the more acidic samples. Some fluoride minerals become more soluble as the pH decreases including fluorapatite (Elrashidi and Lindsay 1986) and the released F^- forms complexes with cations particularly Al^{3+} and Fe^{3+} with these species dominating total F^- activity at pH levels less than 6. Since total aqueous Al and Fe

Table 10. Computer modelled ion difference.

Treatment	Ion Difference(%)^z Mean	Ion Difference(%)^z Range
PG1:S0(60)	19	8.9-32
PG1:S0(80)	21	7.4-34
PG1:S0(U80)	12	7.9-17
PG10:S1(60)	8.3	3.4-17
PG10:S1(80)	11	4.9-33
PG1:S1(60)	7.1	5.2-9.6
PG1:S1(80)	7.2	5.0-11
PG0:S1(60)	15	15-15
PG0:S1(80)	14	14-14

^{z} Expressed as percentage of free cationic charge relative to total cationic charge.

tend to be more abundant at lower pH levels through solubility reactions, they stimulate the release of more F into solution from the solid phase.

Freezing seemed to affect the ion difference, since with freezing the ion difference increased particularly in the acidic samples (Table 10). The samples which were frozen had the near equilibrium conditions obtained at room temperature slightly disrupted and were no longer right at equilibrium with respect to gypsum. Fluoride may play a disproportionate role in the previously frozen samples as it may not precipitate as readily through freezing thus being present to balance out any cations.

In some of the buffered samples the ion difference remained greater than 15% in the PG10:S1 treatment although the means where 8.3 and 11% for the 60 and 80 day harvests respectively. The ion differences for the PG1:S1 and the soil treatments were very consistent among the replicates and ranged only from 5.0 to 15%. In these cases the Cl ion was likely also playing an important role. Halide levels in the till sample are expected to be comparable to average shale F and Cl contents of 600 mg kg^{-1} and 170 mg kg^{-1} respectively (Krauskopf 1979). Only samples 2 and 3 had Cl levels greater than 100 mg kg^{-1} (Table 5) in the phosphogypsum samples from Medicine Hat with a mean level at 200 mg kg^{-1} while the till level was 330 mg kg^{-1}. Two of the phosphogypsum samples having detectable Cl levels (samples 2 and 3) also had ion differences that were high in the frozen PG1:S0 treatment (Appendix II).

Examples of primary percentage speciation of several metals and ligands were provided in Table 11. As pH increased with soil addition, cation complexes with CO_3^{2-} formed which was particularly important for Cr^{3+}, and more NH_3 was also available to react with cations. The percentage of free cation decreased somewhat with

Table 11. Distribution of species (%) in phosphogypsum and soil pore water.

	Free			CO_3^{2-}			NH_3^0			NO_3^-		
Metal	PG[z]	PG/S[y]	S[x]	PG	PG/S	S	PG	PG/S	S	PG	PG/S	S
Al^{3+}	6.99	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ca^{2+}	72.6	64.7	64.3	0.00	0.09	0.50	0.00	0.00	0.00	0.00	0.00	0.00
Cd^{2+}	64.6	53.3	51.1	0.00	0.58	3.42	0.00	0.00	0.83	0.00	0.00	0.00
Cr^{3+}	0.01	0.00	0.00	0.00	100	100	0.00	0.00	0.00	0.00	0.00	0.00
Cu^{2+}	67.8	10.6	0.68	0.00	5.28	6.69	0.00	0.00	0.31	0.00	0.00	0.00
Fe^{3+}	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Zn^{2+}	71.6	52.7	30.2	0.00	0.33	3.69	0.00	0.00	0.00	0.00	0.01	0.00

	OH^-			PO_4^{3-}			SO_4^{2-}			SeO_4^{2-}		
Metal	PG	PG/S	S	PG	PG/S	S	PG	PG/S	S	PG	PG/S	S
Al^{3+}	0.32	100	100	67.8	0.00	0.00	24.9	0.00	0.00	0.00	0.00	0.00
Ca^{2+}	0.00	0.00	0.00	2.30	0.01	0.01	25.1	35.2	35.2	0.02	0.00	0.00
Cd^{2+}	0.00	0.07	0.31	0.07	0.02	0.02	35.3	45.0	44.3	0.02	0.09	0.00
Cr^{3+}	0.00	0.00	0.00	100	0.00	0.00	0.02	0.00	0.00	0.00	0.00	0.00
Cu^{2+}	0.00	76.7	91.8	2.74	0.23	0.07	29.5	7.23	0.47	0.03	0.00	0.00
Fe^{3+}	0.29	100	100	99.6	0.00	0.00	0.05	0.00	0.00	0.00	0.00	0.00
Zn^{2+}	0.00	18.2	49.6	3.65	0.04	0.06	24.7	28.7	16.5	0.02	0.00	0.00

	Free			Al^{3+}			Ca^{2+}			Cd^{2+}		
Ligand	PG	PG/S	S	PG	PG/S	S	PG	PG/S	S	PG	PG/S	S
AsO_4^{3-}	0.00	0.00	0.02	0.00	0.00	0.00	9.44	22.1	12.8	0.00	0.00	0.00
CO_3^{2-}	0.00	0.25	1.07	0.00	0.00	0.00	0.00	2.90	1.56	0.00	0.00	0.00
NH_3^0	0.00	2.45	10.1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
NO_3^-	100	100	100	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
PO_4^{3-}	0.00	0.00	0.00	11.5	0.00	0.00	9.24	18.5	10.1	0.00	0.00	0.00
SO_4^{2-}	68.6	70.6	72.4	1.48	0.00	0.00	29.1	12.7	5.25	0.02	0.00	0.00
SeO_4^{2-}	69.6	70.6	72.4	0.00	0.00	0.00	29.5	12.7	5.25	0.00	0.00	0.00
SeO_3^{2-}	0.00	11.1	23.2	0.00	0.00	0.00	0.02	15.8	13.3	0.00	0.00	0.00
SiO_4^{4-}	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

	Cr^{3+}			Cu^{2+}			Fe^{3+}			H^+		
Ligand	PG	PG/S	S	PG	PG/S	S	PG	PG/S	S	PG	PG/S	S
AsO_4^{3-}	0.00	0.00	0.00	0.02	0.00	0.00	0.00	0.00	0.00	90.4	31.0	15.9
CO_3^{2-}	0.00	0.54	0.12	0.00	0.00	0.00	0.00	0.00	0.00	100	91.8	88.7
NH_3^0	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	100	97.6	89.9
NO_3^-	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
PO_4^{3-}	0.03	0.00	0.00	0.01	0.01	0.00	0.01	0.00	0.00	79.2	41.1	36.2
SO_4^{2-}	0.00	0.00	0.00	0.04	0.00	0.00	0.00	0.00	0.00	0.42	0.00	0.00
SeO_4^{2-}	0.00	0.00	0.00	0.04	0.00	0.00	0.00	0.00	0.00	0.21	0.00	0.00
SeO_3^{2-}	0.00	0.00	0.00	0.02	0.00	0.00	0.00	0.00	0.00	99.9	59.5	27.9
SiO_4^{4-}	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	100	100	100

	Zn^{2+}		
Ligand	PG	PG/S	S
AsO_4^{3-}	0.02	0.00	0.00
CO_3^{2-}	0.00	0.00	0.00
NH_3^0	0.00	0.00	0.00
NO_3^-	0.00	0.00	0.00
PO_4^{3-}	0.02	0.00	0.00
SO_4^{2-}	0.03	0.00	0.00
SeO_4^{2-}	0.03	0.00	0.00
SeO_3^{2-}	0.02	0.02	0.02
SiO_4^{4-}	0.00	0.00	0.00

[z] Sample 1, Rep 1, PG1:S0, 80 days, pH 4.0.

[y] Sample 1, Rep 1, PG1:S1, 80 days, pH 7.5.

[x] Soil, Rep 1, 80 days, pH 8.2.

soil addition and pH increase, and most cations decreased in interaction with PO_4^{3-} and SO_4^{2-} and increased in interaction with OH^-, while Ca^{2+} and Cd^{2+} complexed to a greater degree with SO_4^{2-} after soil addition. The ligands NO_3^-, SO_4^{2-}, and SeO_4^{2-} were mainly in the free ion form, the proportion increasing with neutralisation, while AsO_4^{3-}, CO_3^{2-}, PO_4^{3-}, and SeO_3^{2-} were largely combined with H^+, this proportion of complexing decreasing with neutralisation. Complexing with Ca^{2+} and Mg^{2+} was important for most anions except SiO_4^{4-}, NO_3^- and CO_3^{2-}. Magnesium was not included in Table 10 as it is of minor significance in this study.

4. Comparison with Water Quality Guidelines

Table 12 includes pore water elemental concentrations, pH, electrical conductivity (EC), total dissolved solids (TDS) and Canadian drinking water guidelines (Federal-Provincial Subcommittee on Drinking Water 1989) for those elements or compounds regulated. All PG1:S0(80) and PG1:S0(U80) samples were elevated in Cd relative to drinking water standards (DWS) by at least two orders of magnitude. Selenium values were at least one order of magnitude greater than DWS. Some samples were in excess of the DWS for As, Cr, Cu, Fe, Mn, NO_3^--N, and Zn. A few samples were elevated in Na. The Pb, Ba, and B levels were at or near detection limits. All samples were in excess of DWS for SO_4^{2-}-S (assuming all S measured was SO_4^{2-}-S), and total dissolved solids (TDS). In PG1:S0(U80) all of the samples were at least double the DWS for SO_4^{2-}-S and TDS. The pH range was outside that required for drinking water for both PG1:S0(80) and PG1:S0(U80). The concentration of F would also be expected to exceed DWS at approximately 26 mg L^{-1} (Roberts Thorne 1990) compared to the DWS of 1.0 to 1.5 mg L^{-1}.

In several of the samples the trace elements in the PG10:S1(80) extracts were at or near detection limits (Table 12). Some of the samples had levels of As, Cd and Se that were greater than the DWS by up to over 2 orders of magnitude in the case of Cd. The levels of Mn increased so that the mean and all sample concentrations were at least 1 order of magnitude greater than the DWS. Levels of SO_4^{2-}-S were lower with soil addition but still remained near twice the DWS in all samples, and the pH was closer to an acceptable level but was still out of range. The TDS level remained at least double the DWS in all samples. Some samples of Cu, Na, NO_3^--N and Zn remained in excess of DWS. Those regulated elements near detectable levels were B, Ba, Cr, Fe and Pb and these were considered lower than the DWS.

For PG1:S1(80), some samples of Se and Cd were up to 2 orders of magnitude

Table 12. Comparison of pore water elemental concentrations (mg/L) with drinking water standards.

Element	DL^z	DW^y	PG1:S0(80)		PG1:S0(U80)		PG10:S1(80)		PG1:S1(80)		PG0:S1(80)
			Mean	$Range^x$	Mean	Range	Mean	Range	Mean	Range	Mean
Al	0.2	-	33	13-71	36	13-80	4.3	0.2-10	1.4	0.6-3.5	╪
As	0.03	0.05	+	╪-0.96	+	╪-1.03	+	╪-0.62	+	╪-0.40	0.07
B	0.04	5	+	╪-0.43	+	╪-0.46	+	╪-0.21	+	╪-0.23	╪
Ba	0.005	1	+	╪-0.033	+	╪-0.037	+	╪-0.017	+	╪-0.009	╪
Ca	0.05	-	615.53	419.70-876.10	819.56	604.60-1086.3	422.10	334.50-518.00	248.39	180.00-360.20	116.31
Cd	0.01	0.005	3.64	0.30-9.34	4	0.30-9.34	+	╪-2.35	+	╪-0.23	╪
Co	0.01	-	+	╪-0.05	+	╪-0.06	+	╪-0.05	+	╪	╪
Cr	0.02	0.05	+	╪-0.60	0.28	0.02-0.70	+	╪-0.03	+	╪	╪
Cu	0.01	1	6.56	0.72-20.4	7.29	0.72-22.4	+	╪-1.70	+	╪-0.05	╪
Fe	0.01	0.3	0.48	0.12-1.29	0.57	0.02-1.50	+	╪-0.02	+	╪-0.12	╪
K	0.2	-	110	3.3-290	120	3.4-290	80	3.5-190	45	9.1-110	13
Li	0.04	-	+	╪-0.40	+	╪-0.44	+	╪-0.29	+	╪	0.07
Mg	0.1	-	18	0.6-45	20	0.5-50	88	65-120	260	180-390	330
Mn	0.006	0.05	1.292	0.043-5.047	1.436	0.042-5.507	1.807	0.181-3.522	+	╪-313.8	╪
Mo	0.05	-	+	╪-0.12	+	╪-0.12	+	╪-0.05	+	╪	╪
Na	0.05	200	120	4.90-354	123	5.45-356	109	29.9-223	188	129-293	288
NH_4^+-N	§	-	80.5	1.26-239	80.5	1.26-239	60.4	0.02-169	29	0-109	5.28
NO_3^--N	§	10	13.7	0.15-57.5	13.7	0.15-57.5	8.74	0-39.4	6.72	0-32.7	0.04
Ni	0.03	-	1.46	0.04-3.22	+	╪-3.55	+	╪-1.62	+	╪-0.56	╪
P	0.1	-	520	85-1300	740	84-1700	300	2.1-190	+	╪-310	╪
Pb	0.1	0.01	+	╪	+	╪	+	╪	+	╪	╪
S	0.1	167	391.6	304.9-459.9	534.1	506.7-562.6	405.9	329.4-495.0	612.6	442.5-859.7	636.8
Se	0.3	0.01	2.0	0.5-7.6	2.1	0.4-7.9	+	╪-8.2	+	╪-6.4	╪
Si	0.1	-	10	2.8-23	28	15-40	6.2	4.0-9.4	8.5	3.6-17	3.0
Sr	0.009	-	9.516	6.655-14.29	11.13	8.249-16.00	2.920	2.111-4.684	1.455	0.942-2.096	1.204
Ti	0.01	-	0.03	0.01-0.04	0.04	0.03-0.05	+	╪-0.03	+	╪	╪
V	0.03	-	1.03	0.14-2.84	1.22	0.15-2.99	+	╪-0.20	+	╪-0.03	╪
Zn	0.02	5	16	0.45-36.7	17.6	0.46-40.1	+	╪-10.1	+	╪-0.58	╪
$pH(U)^w$	§	6.5-8.5	3.4	3.0-4.0	3.4	3.0-4.0	5.1	4.3-6.4	6.2	5.1-7.6	8.2
$pH(F)^v$	§	6.5-8.5	3.3	3.0-3.8	╫	╫	4.3	2.2-5.2	6.2	4.7-8.0	8.9
$EC^u(U)$	§	-	3.7	2.2-6.1	3.7	2.2-6.1	3.5	2.4-5.1	4.1	3.4-5.2	3.0
EC(F)	§	-	3.3	1.4-6.1	╫	╫	2.9	1.6-3.5	3.3	2.5-4.3	3.1
$TDS^t(U)$	§	500	2400	1400-3900	2400	1400-2100	2200	1600-3300	2600	3000-5100	1900
TDS(F)	§	500	2100	870-3900	╫	╫	1900	1000-2200	2100	1600-3400	2000

^{z} denotes detection limit; ^{y} drinking water quality guidelines from Federal-Provincial Subcommittee on Drinking Water (1989) ; ^{x} range of all samples and replicates; ^{w} denotes samples left unfrozen prior to analysis; ^{v} denotes samples frozen prior to analysis; ^{u} electrical conductivity in dS/m; ^{t} total dissolved solids in mg/L calculated from EC (TDS=640*EC)(Bohn *et al.* 1985); ╪ denotes content below detection limit; + denotes incomplete data set; § denotes data unavailable; - denotes no limit set; ╫ denotes parameter does not apply.

in excess of DWS although many samples were at the detection limit (Table 12). In some samples As levels exceeded DWS by nearly 1 order of magnitude but levels decreased from PG10:S1 and many samples were at or near the detection limit. Manganese levels were quite stable with soil additions with the highest sample remaining in excess of DWS by nearly 4 orders of magnitude in the PG1:S1(80) treatment. Some samples of NO_3^--N and Na remained in excess of the DWS. Boron, Ba, Cr, Cu, Fe and Pb remained near detectable levels and were considered lower than the DWS. Levels of SO_4^{2-}-S and TDS remained at least double the DWS, while the pH was just outside of the acceptable range. For the PG0:S1(80), Na and SO_4^{2-}-S were in excess of the DWS. The level of TDS was 4 times in excess of the DWS. The remaining regulated elements measured were at or near the detection limit and were considered lower than DWS.

Decreases in the levels of NO_3^--N, As, and Se with soil addition were not considered significant, preventing treatment comparisons, as they did not account for a great deal more than the expected effects of the simple dilution of phosphogypsum with soil as the total phosphogypsum in the system was decreased by 50% from PG1:S0(80) to PG1:S1(80). Decreases considered significant were those where there was a decrease by greater than 2 times.

The tendency for Mn levels to be unrelated to pH corresponds to a leaching column study by Wangen and Jones (1984) in which it was found that elemental retentions were substantial for all species except Mn which was eluted in excess from all soils except the most calcareous. The DWS for Mn is quite low for aesthetic reasons as undesirable effects on taste, staining of laundry and discolouration of water may start at 0.15 mg L^{-1} (De Zuane 1990). However, it is very unlikely that Mn would be a health hazard in typical, expected concentrations in raw and drinking water. In fact, Mn has been judged as one of the least toxic elements.

E. Solubility Equilibria Relationships

The geochemical processes controlling long term elemental concentrations in all waste leaching environments are precipitation/dissolution, redox speciation and adsorption/desorption (Eary *et al.* 1990). If a solubility controlling solid for an element is present in a waste or if such a solid can precipitate when meteoric waters contact the waste then adsorption/desorption reactions can be neglected. Thus, in this case, long term aqueous concentrations of the element can be predicted using the appropriate thermodynamic data. Thermodynamic applications typically require the assumption of chemical equilibrium which may seem simplistic in a dynamic waste leaching environment but many secondary solids precipitate rapidly, once the surrounding solution is saturated, including hydroxides, carbonates, sulphates and sulfides.

Although the thermodynamic data for many pure-phase secondary solids are available, the thermodynamic method is somewhat restricted as few data are available for solid solutions (Eary *et al.* 1990). Furthermore, adsorption/desorption reactions can become major processes affecting concentrations when solubility controlling solids are absent or are slow to precipitate or dissolve due to kinetic factors. In addition, if an element is stable in more than one oxidation state in the environment, the redox conditions or causes of redox transformations must be known, because both precipitation/dissolution and adsorption/desorption are dependent on elemental oxidation state.

In this section ion activities generated by GEOCHEM from entered elemental analyses of equilibrated pore waters have been related to theoretical levels predicted using solubility constants for potential solubility controlling solids. A subset of elements analysed in the pore water extractions were selected to be examined with relationship to potential solubility controlling solids. Elements were selected based on their abundance, environmental consequence, relationship to other elements of environmental concern and availability of thermodynamic data on potential solubility controlling solids. Thus, the set of elements selected was made up of: Al, As, Ca, Cd, Cr, Cu, Fe, P, S, Se, Si, and Zn.

Aluminium, Ca, Fe, P, S, and Si were considered a subset of the major elements. All of these elements were present in the solid phase at concentrations greater than 200 mg kg^{-1} although not all were present in solution at high concentrations. Information on the major elements was necessary for the development of equilibria isolines for the trace element solid phases. Furthermore, some of the major elements are also of environmental consequence such as SO_4^{2-}-S and Fe, both of which are regulated in drinking water (Federal-Provincial Subcommittee on Drinking Water 1989); P has been indicted as a cause of eutrophication in surface waters (De Zuane 1990).

Trace elements examined included As, Cd, Cr, Cu, Se, and Zn. Cadmium and Se were selected because of their elevated levels in this material and their extreme toxicity (De Zuane 1990). Copper and Zn were included as they behaved similarly to Cd but occurred at greater concentrations thus potentially serving as models for the less abundant but more toxic element and both were elevated relative to drinking water standards (DWS) in some sample extracts. Arsenic and Cr were not enriched in the solid phase but were identified as elements of potential environmental concern at low levels if readily released from the material. These two elements were also elevated relative to DWS in some of the sample extracts. Chromium was of particular interest because of the availability of solid phase thermodynamic data including those for a solid solution (Rai *et al.* 1987a). Berish (1990) identified both Cr and As as trace elements of environmental concern in phosphogypsum. Elevated levels of As in other stacks have been documented (May and Sweeney 1980), although the element was not enriched at this site.

1. Major Elements

i. Calcium and Sulphur

These two elements were discussed together because of their expected dependency on gypsum solubility in most of the systems under study. The gypsum solubility equilibrium isoline along with data from the 80 day incubation including the set of unfrozen samples from the PG1:S0 treatment have been included in Figure 32. The extracts left unfrozen were at or near saturation relative to gypsum as they occurred right on or near the solubility equilibrium isoline. This provided evidence that in the PG1:S0 system, Ca^{2+} and SO_4^{2-} activities were controlled by gypsum. The importance of gypsum as a solubility controlling solid in phosphogypsum was expected as it has been established as the dominant mineral making up the material.

With freezing most of the samples of phosphogypsum alone decreased in activity of both SO_4^{2-} and Ca^{2+} becoming slightly undersaturated relative to gypsum based on thermodynamic data for the equilibrium relationship developed at 298°K (Fig. 32). Although samples were given at least 24 hours to equilibrate to room temperature, in the absence of the agitation required to expose all crystal surfaces to the solution, the residue persisted.

In the PG10:S1 treatment there was an increase in SO_4^{2-} activity in most samples, but it was combined with a decrease in Ca^{2+} activity producing an undersaturated condition relative to gypsum (Fig. 32). The PG1:S1 system samples were somewhat more undersaturated relative to gypsum, and although they had greater SO_4^{2-} activities than the other phosphogypsum systems, they had lower Ca^{2+} activities. The decrease in Ca^{2+} activity with soil addition was likely a result of $CaCO_3$ precipitation and/or adsorption processes. Freezing may also have affected

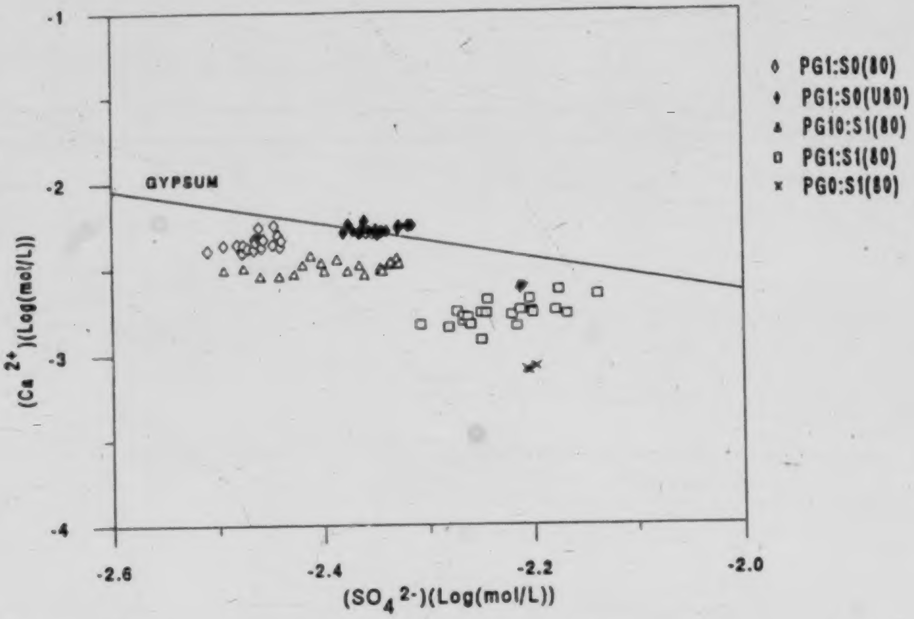

Figure 32. Gypsum solubility eqilibrium with data from 80 day incubation.

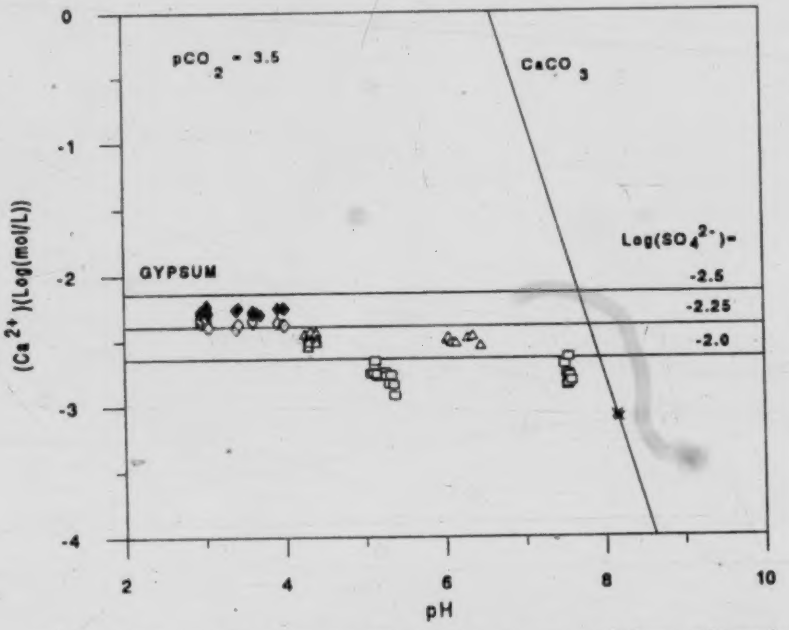

Figure 33. Solubility equilibria for some calcium minerals with data from 80 day incubation.

Thermodynamic data from Lindsay (1979).

these systems producing undersaturation.

It is evident that $CaSO_4*2H_2O$ and $CaCO_3$ were coexisting in the PG10:S1 and PG1:S1 systems. At pH levels less than about 7.5 to 8.0, the Ca^{2+} activity should theoretically be controlled by gypsum (Fig. 33), but if all of the $CaCO_3$ had not converted to gypsum due to kinetic or physical constraints a different outcome was possible. In soils, between pH 7.5 and 8.0, gypsum and calcite can coexist (Lindsay 1979). In fly ash, gypsum and calcite have also been adopted to set the upper limits on aqueous concentrations of Ca and S (Mattigod *et al.* 1990). However, one would expect $CaCO_3$ to produce a very high level of Ca^{2+} activity below pH 7.5, thus it is likely that adsorption on solid surfaces including onto $CaCO_3$ was occurring which maintained the Ca^{2+} activity at an undersaturated level relative to gypsum.

The PG0:S1 treatment extracts were also undersaturated relative to gypsum. From Figure 33 it is evident that the soil was saturated relative to $CaCO_3$. No freezing induced precipitate was observed in the soil alone treatment extracts. This information establishes that freezing induced precipitation of $CaCO_3$ did not occur.

Although in Figure 33 it appears as though the PG10:S1 treatment samples fell within the gypsum saturation range, they actually were undersaturated as their log SO_4^{2-} activities were in the range of -2.3 to -2.5 (Fig. 32). The PG1:S1 treatment sample extracts were similarly undersaturated as their log SO_4^{2-} activities were in the range of -2.1 to -2.4.

Using the information obtained it would not be difficult to estimate the concentrations of S or Ca that would leach from a phosphogypsum system. The concentration of the free ion can be calculated using the Davies equation if ionic strength estimates are available (Davies 1962). To estimate the total concentration, information on the activities or concentrations of other major ions or elements and the ionic strength are required, from this speciation could be performed in reverse to obtain concentrations or forward by trial and error using estimates of concentrations for Ca and S until the free ion activities governed by gypsum solubility were obtained. Furthermore, many geochemical models, including GEOCHEM, allow the option of imposing one or more solid phases during a computer run, thus, if gypsum was known to be a solubility controlling solid, it could be imposed and modelled concentrations of Ca and S under different chemical equilibria conditions could then be obtained. A similar procedure could be used whenever a solubility controlling solid for an element has been identified.

This application of thermodynamics to understand the controls on Ca and S concentrations demonstrates the importance and applicability of this approach. The example of gypsum and calcite was particularly appropriate as it followed expected theoretical trends especially in the phosphogypsum and soil alone treatments and in the absence of a freezing induced residual precipitate. In cases such as this, the solubility controlling solids were well established, since the indirect predictions were supported by the identification, as discussed in previous sections, of the solids by other more direct means.

ii. Phosphorus

The solubility equilibria diagram for phosphorus minerals was drawn using $H_2PO_4^-$ activity as this ion is the dominant form of phosphorus in the pH range from 3.5 to 6.5 (Lindsay 1979) which is the range in which most of the samples fell (Fig. 34). Calcium ion activity was obtained from the mean level among all samples and fluoride activity was calculated by assuming equilibrium with fluorite (CaF_2) (Jenne *et al.* 1980; Lindsay 1979; Murray and Lewis 1985). All of the PG1:S0(80) treatment samples fell below the fluorapatite ($Ca_5(PO_4)_3F$) (FA) isoline. Some of the samples were slightly undersaturated relative to FA while those falling right on the line were at saturation. The points were distributed with a similar slope to FA providing some evidence that this mineral was controlling $H_2PO_4^-$ activity in this system. Fluorapatite is the phosphate mineral of all sedimentary marine phosphate deposits (MacDonald 1987). Therefore, any residual mineral phosphorus present in phosphogypsum would be expected to be present as FA.

Once the phosphogypsum was mixed with soil in both the PG10:S1 and PG1:S1 treatment, the set of seven samples clustered into two groups, one less buffered and thus of higher pH (samples 1, 4, and 6) and one more buffered and thus at a lower pH (samples 2, 3, 5, and 7) (Fig. 34). This behaviour was similar to what was observed when buffering curves for these samples were developed by titrating with 0.1 N NaOH (Fig. 3 and 4).

The less buffered set of samples for the PG10:S1 treatment distributed below and with a similar slope to the hydroxyapatite ($Ca_5(PO_4)_3OH$) (HA) isoline and above the FA isoline (Fig. 34). Hydroxyapatite may have been a solubility controlling solid in this case although the points were also located below the dicalcium phosphate ($CaHPO_4$) (DCP) and dicalcium phosphate dihydrate ($CaHPO_4{*}2H_2O$) (DCPD) isolines. The rest of the phosphogypsum-soil mixes distributed below and with a similar slope to the ß-tricalcium phosphate (β-$Ca_3(PO_4)_2$) (ß-TCP) line indicating that it may be a solubility controlling solid in these systems. However, the less buffered

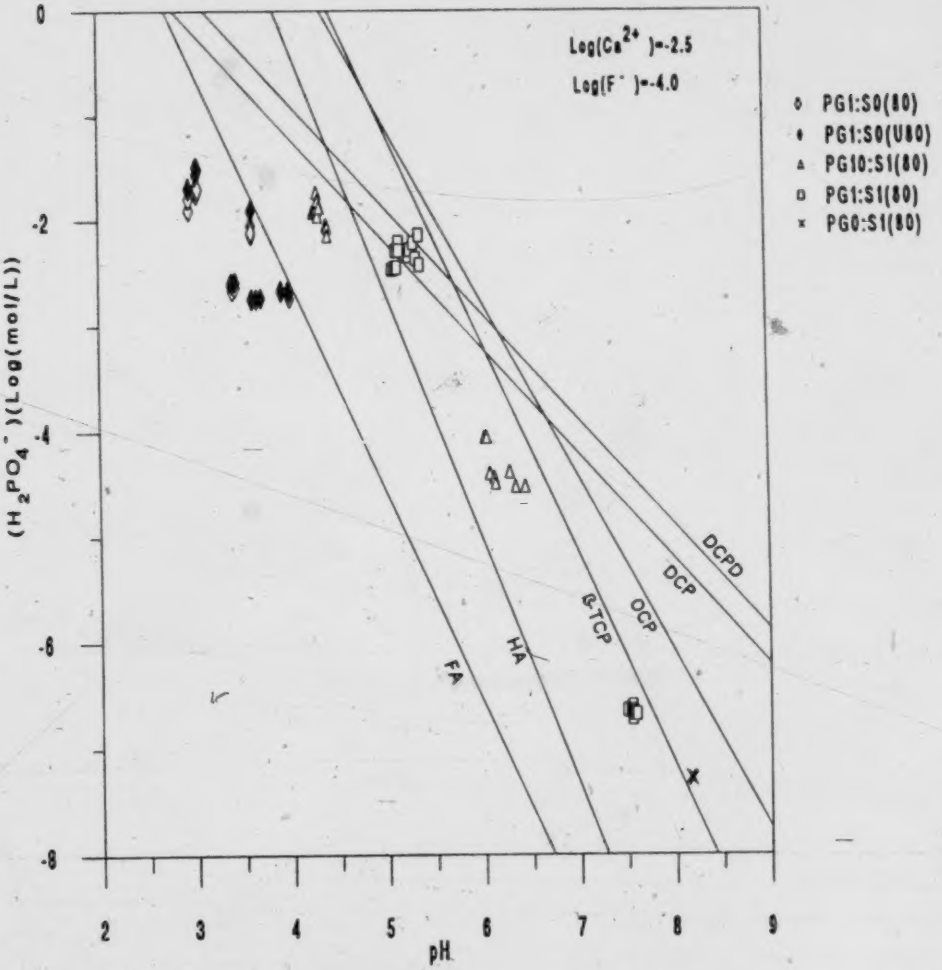

Figure 34. Solubility equilibria of some phosphate minerals with data from 80 day incubation.

Thermodynamic data from Lindsay (1979).

samples of the PG1:S1 treatment clustered on the DCP and DCPD isolines. The presence of octacalcium phosphate ($Ca_4H(PO_4)_3{*}2H_2O$) (OCP) was also not ruled out as its isoline falls just above that of ß-TCP. The $H_2PO_4^-$ activity in the extract from the soil alone treatment fell near but just above the ß-TCP line in support of the presence of ß-TCP as a solubility controlling solid.

It seems likely that in the phosphogypsum alone system, FA was the solubility controlling solid for phosphorus, while in the soil mixes, a set of phosphorus minerals may coexist. It has been noted in soils, that in the pH range from 6.0 to 6.5, several of the phosphate minerals can coexist including DCP, DCPD, OCP and ß-TCP all of which tend to maintain approximately $10^{-3.25}$ M $H_2PO_4^-$ activity in this pH range (Lindsay 1979). There was no evidence for the existence of varisite ($AlPO_4{*}2H_2O$) or strengite ($FePO_4{*}2H_2O$) in the systems studied although they have been suggested as potential solubility controlling solids in highly acid soils (Lindsay 1979). From the information obtained, the equilibrium pore water P concentration in a phosphogypsum or in a phosphogypsum-soil system can be estimated at a given pH assuming cation exchange capacity remains constant and amounts of other major ions and ionic strength are known.

iii. Aluminium

Aluminium was modelled graphically using the free ion form although at pH levels greater than about 4.5 most of the Al tends to be complexed with OH^- (Lindsay 1979) (Fig. 35). The study of Al in the various treatments and its speciation was somewhat cursory as F^- interactions were not examined in this work. Fluoride aluminium complexes can dominate Al speciation; for example, in a soil at pH 6 in equilibrium with gibbsite with 10^{-4} M F^- concentration, the soil F^- complexes can increase the soluble Al by approximately 60 fold (Lindsay 1979). Even with these restrictions the computer estimated free ion activity of Al followed distinct theoretically predictable trends supporting the presence of some aluminium sulphate minerals.

All of the PG1:S0 and PG10:S1 samples fell on or near to the jurbanite ($AlOHSO_4{*}5H_2O$) isoline with those at the lower pH also falling near the alunite ($KAl_3(OH)_6(SO_4)_2$) isoline (Fig. 35). Either or both of these minerals were thus predicted to occur in these systems. The PG1:S1 treatment extracts fell near but undersaturated relative to the alunite and basaluminite ($Al_4(OH)_{10}SO_4{*}5H_2O$) isolines. The less buffered cluster of PG1:S1 samples was also near but undersaturated relative to the gibbsite ($Al(OH)_3$) isoline. The soil extract replicates were slightly

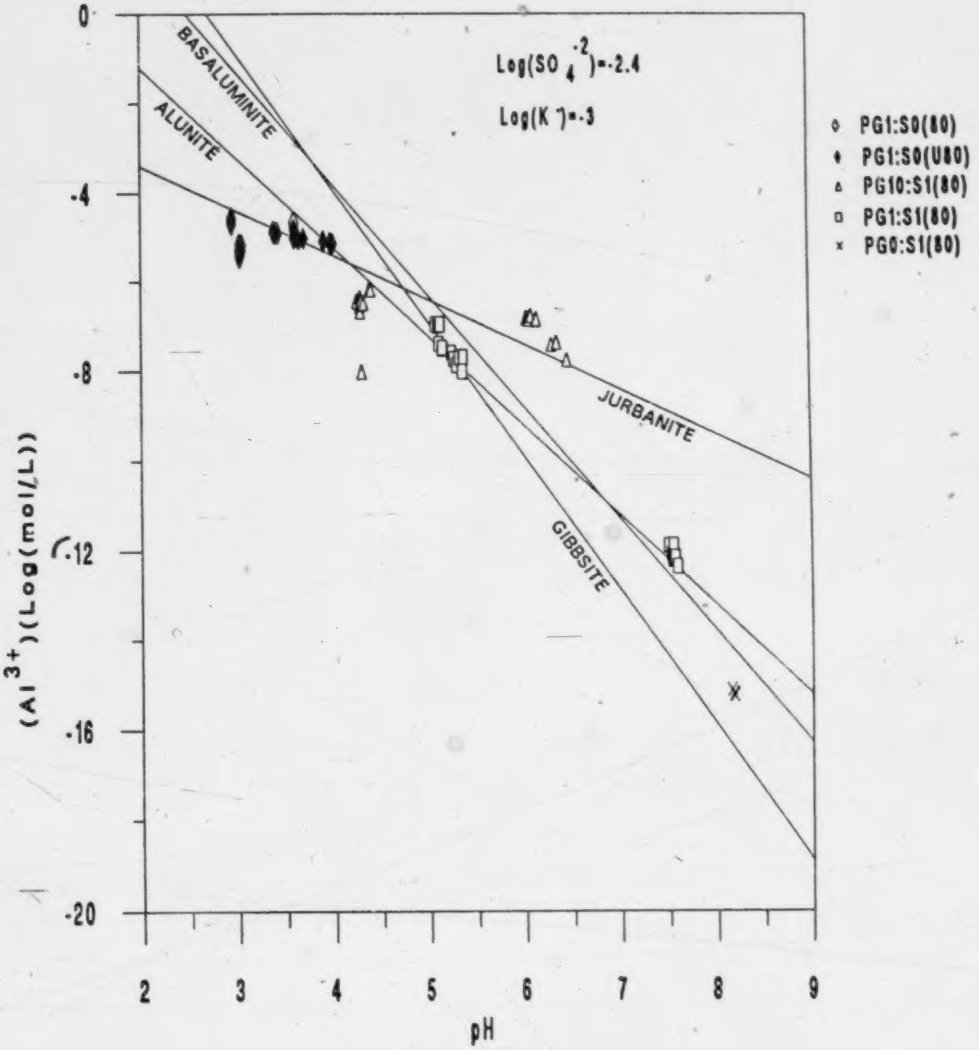

Figure 35. Solubility equilibria for some aluminium minerals with data from 80 day incubation.

Thermodynamic data from Linsday (1979) and Sposito (1989).

supersaturated relative to gibbsite.

This evidence suggests that jurbanite and alunite existed in the in the PG1:S0 and PG10:S1 system and that basaluminite, alunite and gibbsite were present in the in the PG1:S1 treatment samples. In the soil alone, gibbsite or possibly basaluminite was the predicted solubility controlling solid.

The trends observed for Al in this study correspond to those in related research. Although gibbsite has been used in fly ash to set upper limits on aqueous concentrations of Al (Mattigod *et al.* 1990), according to Rai *et al.* (1987a), in acid conditions in fly ash, gibbsite or $AlOHSO_4$ are expected to limit Al^{3+} activity in the solution phase. Alumino sulphate minerals including alunite and basaluminite have been predicted to form in some soils and sediments (Adams and Rawajfih 1977; Nordstrom 1982b; Singh and Brydon 1969). These sulphate minerals are more stable than gibbsite at relatively low pH values (<4) and high sulphate activities ($>10^{-3}$) (Lindsay 1979; Sposito 1989). However, in Nordstrom's (1982b) study, although basaluminite was kinetically favoured to precipitate in waters containing sulphate, it was found to be unstable for all values of pH and sulphate activity. In another study, when phosphogypsum was reacted with a highly weathered acid soils, the formation of $AlOHSO_4$ and alunite phases was predicted in one of the samples as the solution was supersaturated relative to these two minerals (Alva *et al.* 1990). Alunite (O'Brien and Sumner 1988) and alunite and basaluminite (Alva et al. 1991) have been suggested as forming in other studies under similar conditions.

iv. Iron

In the systems studied, iron was assumed to be completely oxidised, remaining in the Fe^{3+} form, and the free ion activity was used for the creation of a solubility diagram although at pH values greater than approximately 3.5, most aqueous Fe is complexed with OH^- (Lindsay 1979) (Fig. 36). Dissolved Fe concentrations were expected to be controlled primarily by the Fe(III) solids in the oxygenated systems maintained in this study. In general in leaching environments, aqueous concentrations of Fe have been observed to be controlled primarily by precipitation/dissolution reactions, not by adsorption/desorption reactions (Rai *et al.* 1987a). As in the case of Al^{3+}, at low pH values, F^- complexes have been recorded as dominating Fe^{3+} activity (Rai *et al.* 1984) introducing some error into the present predictions developed in the absence for F measurements. However, Fe^{3+} activities behaved in a thermodynamically predictable manner comparable to the behavior of Al^{3+} activities.

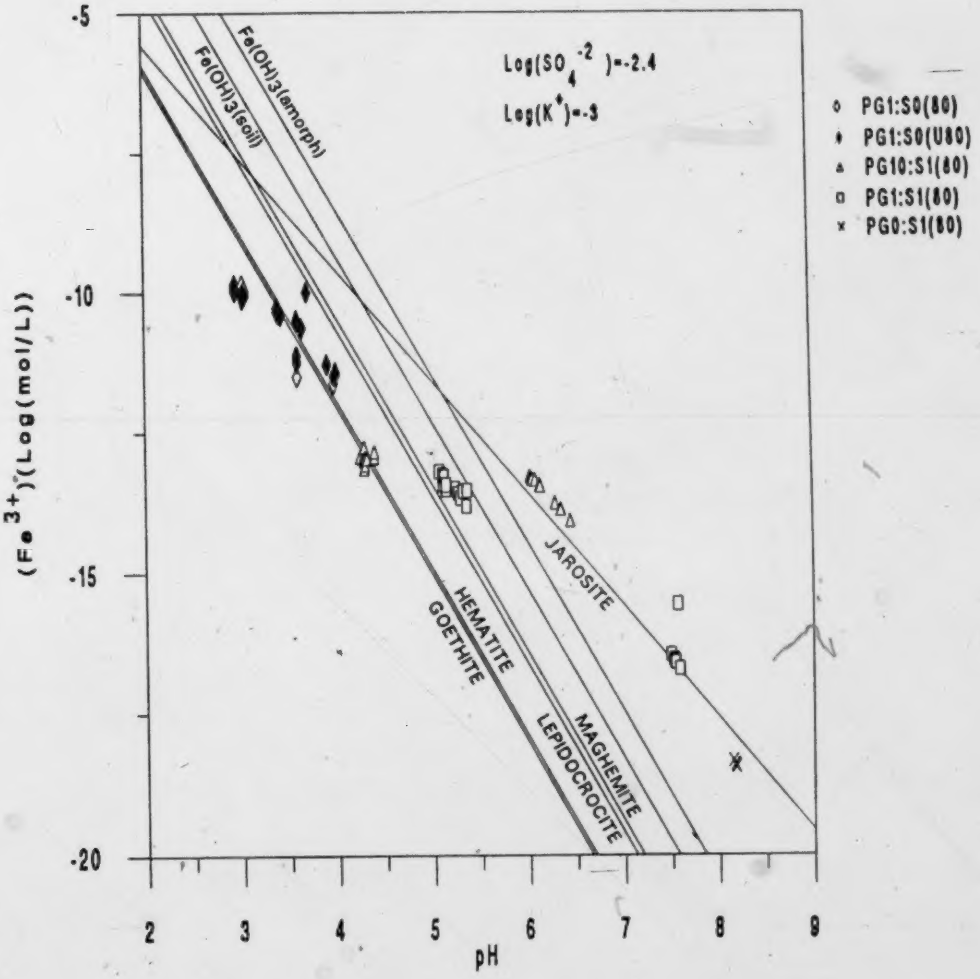

Figure 36. Solubility equilibria for some iron minerals with data from 80 day incubation.

Thermodynamic data from Lindsay (1979).

Jarosite ($KFe_2(SO_4)(OH)_6$), a sulphate mineral, was found to be important in predicting Fe(III) free ion activity in most of the systems studied.

In the phosphogypsum alone treatment and in the more buffered samples of the of the PG10:S1 treatment, Fe^{3+} activities distributed along the goethite (α-FeOOH) or hematite (α-Fe_2O_3) isolines (Fig. 36). Under conditions in most aerobic soils goethite is expected to be the most stable phase (Schwertmann and Taylor 1989). In fossil fuel waste leaching environments, at pH levels greater than 4, goethite and hematite were predicted as the least soluble potential solubility controlling solids that contain Fe (Rai *et al.* 1987a). But, often the most stable phase does not form the solubility controlling solid due to sluggish kinetics leading to an infinitely slow transformation of metastable into stable phases (Schwertmann and Taylor 1989). Thus metastable phases such as ferrihydrate (Fe_2O_3*$9H_2O$) and lepidocrocite (γ-FeOOH) may exist in soils over a pedogenic time scale.

The more buffered samples of the PG1:S1 treatment fell between the maghemite (γ-Fe_2O_3) and the soil $Fe(OH)_3$ isolines (Fig. 36). These isolines occurred just below that of amorphous $Fe(OH)_3$. Soil $Fe(OH)_3$ has been defined by Lindsay (1979) as an amorphous phase having a greater degree of structural order than freshly precipitated amorphous $Fe(OH)_3$. Amorphous $Fe(OH)_3$ was adopted in this study as the best solubility controlling solid for secondary application in trace element diagrams because the existence of soil $Fe(OH)_3$ has not been well established. In some fly ash samples, Roy and Griffin (1984) showed that computed Fe^{3+} activities were in equilibrium with $Fe(OH)_3$.

The less buffered samples of the PG10:S1 and PG1:S1 treatments as well as samples from soil alone treatment fell along or near to the jarosite isoline and distributed with a slope very close to that of jarosite providing strong evidence for the dominance of this mineral as a solubility controlling solid in these systems. Jarosite has been identified as a weathering product in acid mine drainage environments (Nordstrom 1982a) and through the leaching of copper sulphide mine tailings (Murr 1980). It has also been established as a solubility controlling solid in acidic systems containing activities of K^+ and SO_4^{2-} that reach 10^{-3} M (Rai *et al.* 1987a). Thus, amorphous $Fe(OH)_3$, goethite, hematite and jarosite have been predicted as solubility controlling solids for Fe in the systems under study.

v. Silicon

Although $H_4SiO_4^0$ was expected to be the dominant Si complex in solutions in the pH range of interest (Lindsay 1979), the highest level of hydrogen complexing modelled in GEOCHEM was $H_2SiO_4^{2-}$ so it was assumed that the activities of modelled $H_2SiO_4^{2-}$ were equivalent to the $H_4SiO_4^0$ activities for the formation of a solubility equilibria diagram (Fig. 37). Along with effects on Fe and Al, aqueous F levels also affect Si speciation because at low pH fluorosilicate complexions such as SiF_6 form (Sillen and Mantell 1964).

Estimated activities of $H_4SiO_4^0$ varied widely, apparently independently of pH, as samples of the same pH could vary in $H_4SiO_4^0$ activity by up to 3 times (Fig. 37). However, there was a well-defined upper limit to the values showing an inverse relationship to pH. In all samples the activity of $H_4SiO_4^0$ distributed between the quartz and amorphous silica isolines. The phosphogypsum alone samples were close to the amorphous silica isoline line but were somewhat undersaturated. In the phosphogypsum-soil mixes the extracts were closer to the quartz solubility equilibrium isoline but were supersaturated in most cases. One of the frozen PG1:S0 samples and the soil samples fell on the quartz line. Freezing had a large effect on the $H_4SiO_4^0$ activity lowering it substantially. Likely an amorphous silica solid precipitated with the gypsum and it did not obtain equilibrium with thawing.

Quartz has been established as the most thermodynamically stable form of Si under normal temperature and pressures (Lindsay 1979) but its formation may not always be favoured kinetically and thus levels of $H_4SiO_4^0$ activity maintained in soils have been measured to be intermediate between those maintained by amorphous silica and quartz. The same distribution occurred in the phosphogypsum and phosphogypsum-soil mixes. Quartz was present in phosphogypsum samples as it has been detected by x-ray diffraction and observed by scanning electron microscopy, and quartz was also present in the soil samples as it is known to be the most stable of all of the more abundant primary minerals (Hausenbuiller 1985) and thus dominates the sand size fraction. However, amorphous silica could be used to estimate upper limits for Si concentrations in phosphogypsum leachate as it has rapid dissolution-precipitation kinetics and has been suggested as a mineral for setting upper limits on aqueous silicon levels in fossil fuel wastes (Rai *et al.* 1987a).

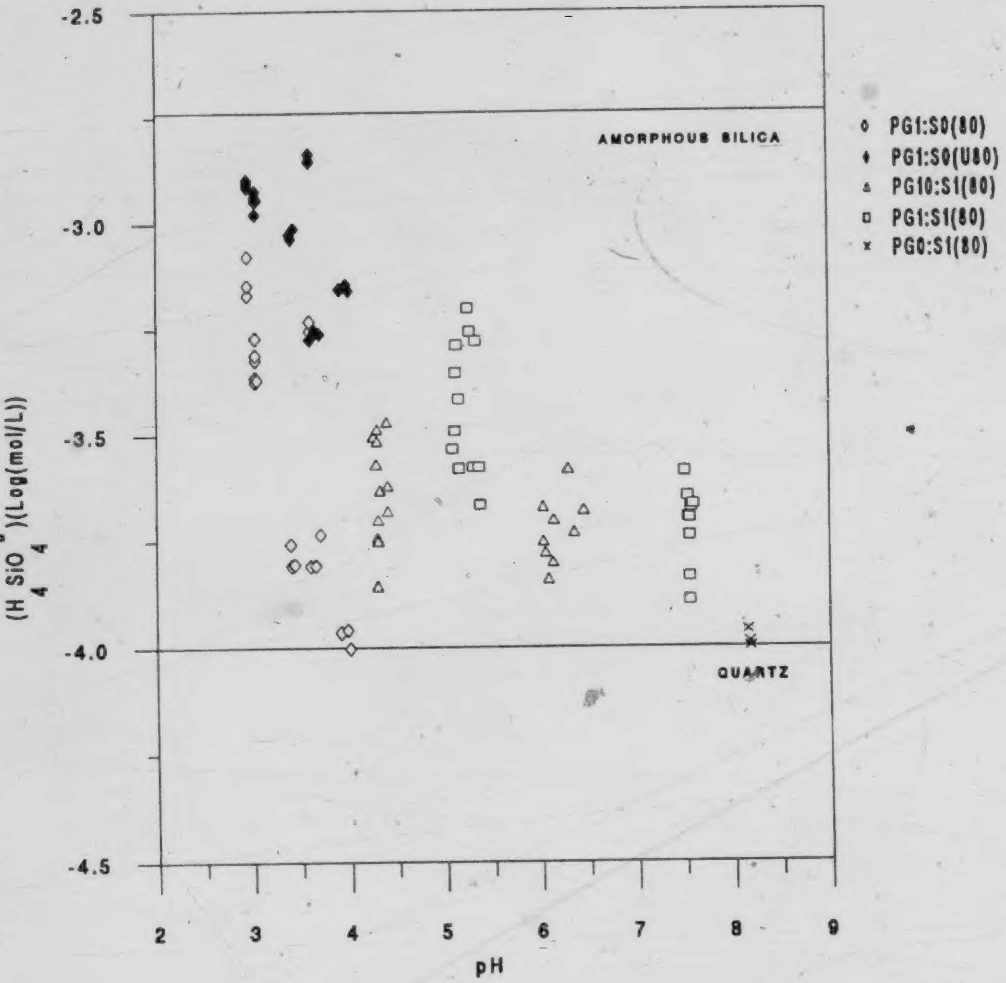

Figure 37. Solubility equilibria for some silica minerals with data from 80 day incubation.

Thermodynamic data from Lindsay (1979).

2. Trace Elements

i. Cadmium, Copper and Zinc

Cadmium, Cu and Zn behaved similarly in the systems under study. In near neutral to acidic solutions the predicted solids containing these three elements have been shown to be relatively soluble, and it is likely that adsorption reactions may exert principal controls on the elemental concentrations under such conditions (Eary *et al.* 1990). However in slightly acidic to alkaline conditions, concentrations of Cd, Cu and Zn have been predicted to be limited by the solubilities of various sulphate, carbonate and oxide solids including $CdCO_3$, $CuO/Cu_3SO_4(OH)_4$, $ZnO/Zn_5(OH)_6(CO_3)_2$. Their phosphate minerals governed by fluorapatite (FA), hydroxyapatite (HA), ß-tricalcium phosphate (ß-TCP) and octacalcium phosphate (OCP) were considered in this study along with potential carbonate, hydroxide and oxide solids. Sulphate minerals were not considered because of their high solubility making them unlikely candidates for solubility controlling solids in the pH range of interest (Lindsay 1979).

None of the elements showed any trends close to the potential solubility controlling solids depicted with Cu showing some relationship to the CuO isoline when the pH was greater than 7 in the less buffered PG1:S1 treatment samples and in the soil alone treatment replicates (Fig. 38-40). The slope was close to that of CuO but the samples remained slightly undersaturated. However, for each element the free ion activity showed a strong negative relationship with pH with the activity decreasing by 3 orders of magnitude as pH increased from 3 to 8 in the case of Cd and Zn and by over 4 orders of magnitude in the case of Cu. In each case, at least a portion of the PG1:S0 and the more buffered PG10:S1 samples fell near or at the confluence of the respective phosphate mineral isolines governed by ß-TCP, HA, and OCP. It is difficult to come to any predictions for this cluster as the distribution of points does not follow a definite slope or if any slope is evident as in the case of Cu it is not like that of $Cu_3(PO_4)_2{*}2H_2O$ but rather more like those of copper oxide, hydroxide and carbonate.

As expected, in the acidic pH range it was difficult to predict solubility controlling solids for any of these elements. However, it was probable, based on the strong negative distribution relative to pH, that a solubility controlling solid was present. Adsorption can also reduce solution ion activities as pH increases for these elements (Rai *et al.* 1987a), but in this study, adsorption/desorption was expected to be limited by the low cation exchange capacity. It was possible that solid solutions served

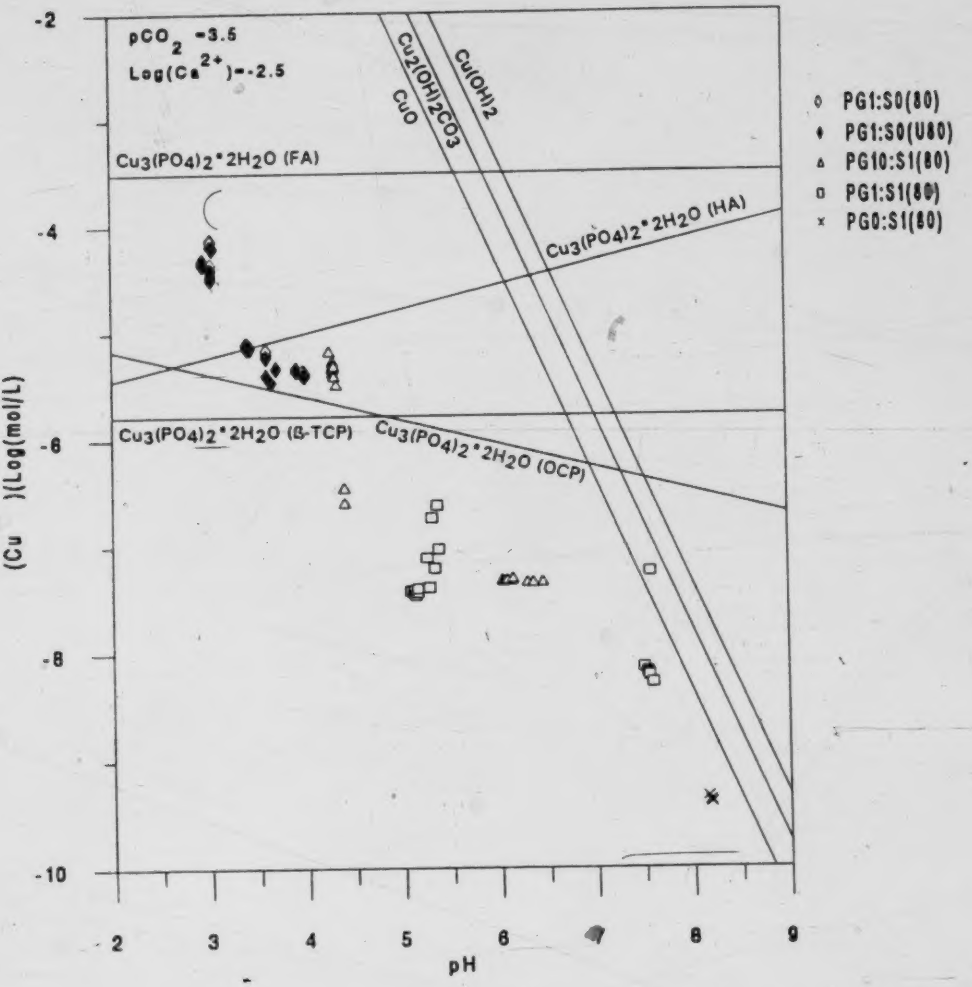

Figure 38. Solubility equilibria for some copper minerals with Data from 80 day incubation.

Thermodynamic data from Lindsay (1979).

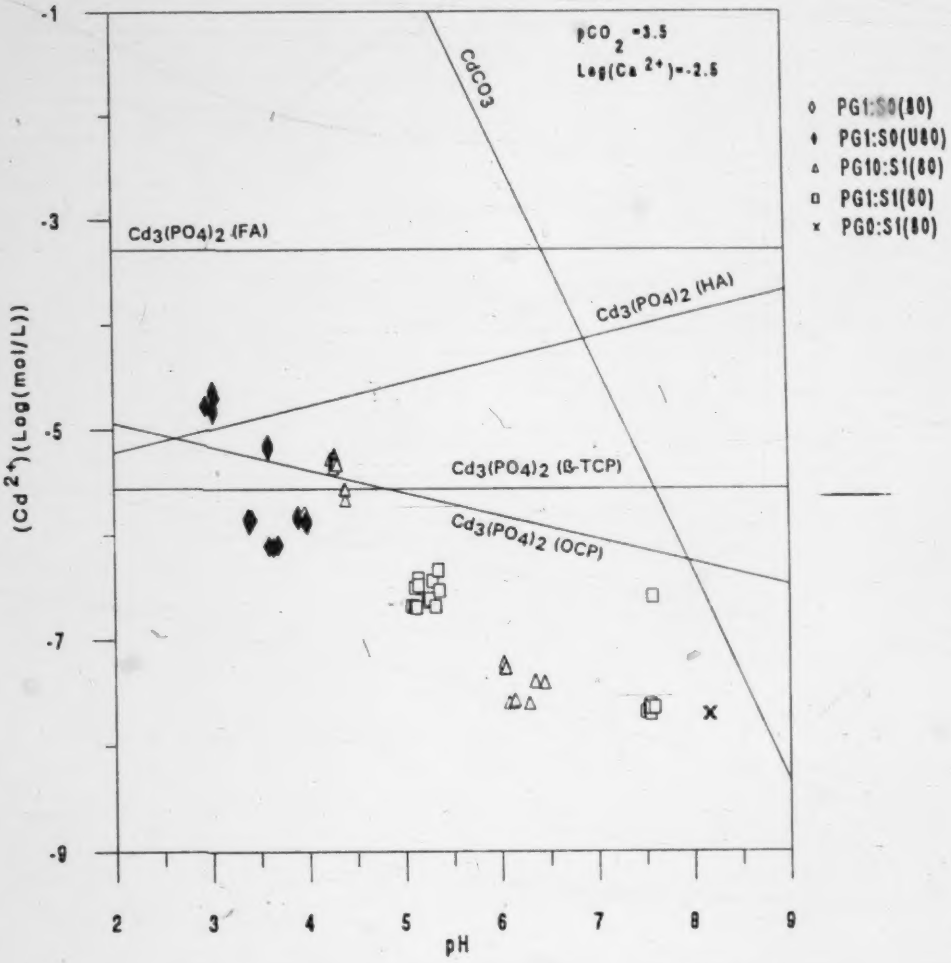

Figure 39. Solubility equilibria for some cadmium minerals with data from 80 day incubation.

Thermodynamic data from Lindsay (1979)

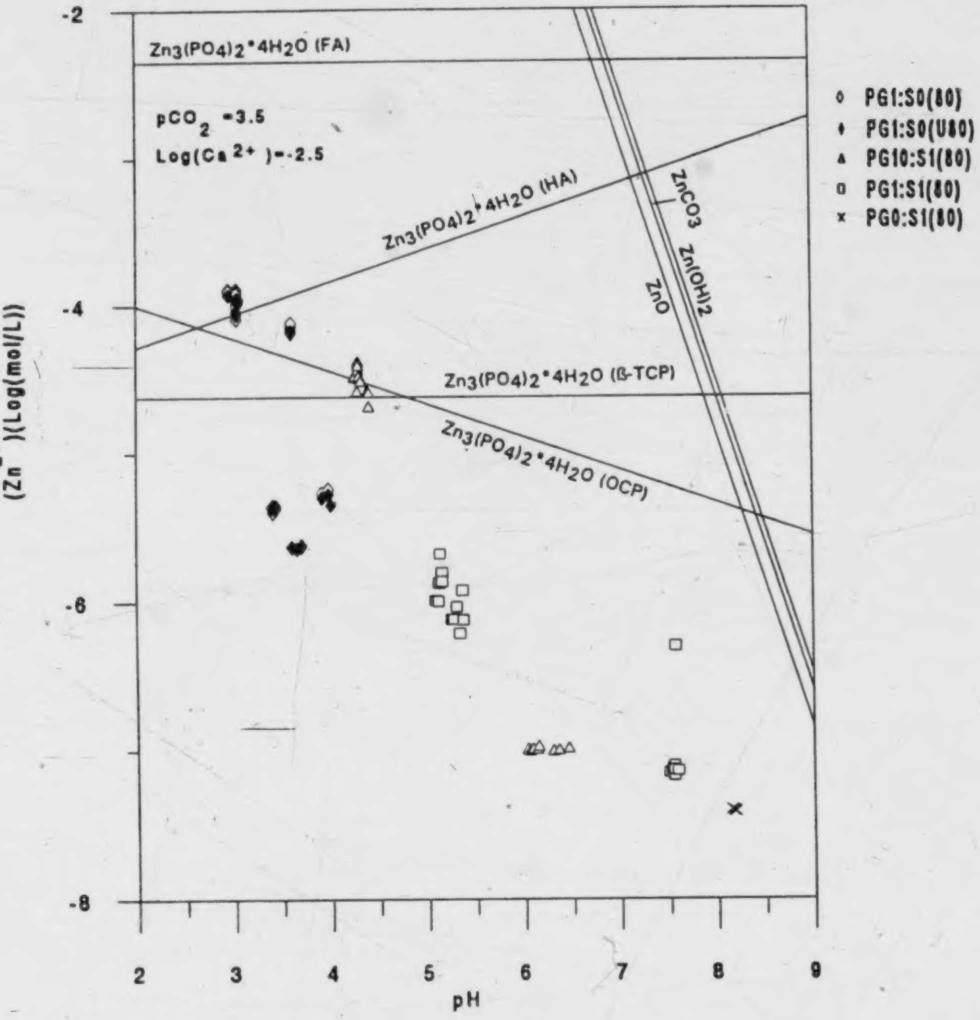

Figure 40. Solubility equilibria for some zinc minerals with data from 80 day incubation.

Thermodynamic data from Lindsay (1979).

as solubility controlling solids but the thermodynamic data on solid solutions is lacking (Eary *et al.* 1990). Also, clay or carbonate mineral surfaces in the systems where soil was present may have acted as nucleation sites for precipitating trace elements as implicated by Dhillon *et al.* (1981). They observed that, at Cu additions of less than 100 μM, alkaline systems were undersaturated relative to $Cu(OH)_2$ and $Cu_2(OH)_2CO_3$.

It was not possible to establish an estimate for maximum attainable solution concentrations from the information available without the establishment of solubility controlling solids. If an experiment was conducted in which the slurry was spiked with one or more of these elements and solution concentrations were observed, one could then predict solubility controlling solids if they exist (Rai and Szelmeczka 1990). On average, based on oven dry weight, the phosphogypsum samples contained 20 mg kg^{-1} Cd, 40 mg kg^{-1} Cu and 80 mg kg^{-1} Zn. Even if all of this dissolved from 300 g of phosphogypsum into 600 g of water, the maximum concentration attainable in log(mole L^{-1}) would be -4 Cd, -4 Cu and -3 Zn. Thus in the phosphogypsum alone samples, a large proportion of these trace elements was in solution, making it impossible for solution activities to reach the phosphate mineral isoline when governed by fluorapatite or the carbonate, hydroxide or oxide mineral isolines at the low pH range. For all of these elements, the samples with pH levels greater than 7 were at or near the detection limit. In the case of Cu, the reason that there is a definite slope present at this high pH range is attributable to speciation as most Cu converted to a complexed form with hydroxide in this pH range.

Studies of Cd precipitation suggest that in alkaline soils $CdCO_3$ and $Cd_3(PO_4)_2$ or a mixed compound occur as solubility controlling solids for Cd (Street *et al.* 1977; Santillan-Medrano and Jurinak 1975). In general at pH levels greater than 6, $CdCO_3$ controls Cd concentration in alkaline soils (Cavallaro and McBride 1978; McBride 1980; Street *et al.* 1977, 1978), mine tailings (Jenne *et al.* 1980), and landfill leachates (Frost and Griffin 1977b). Precipitation of Cd in a calcium sulphate based solid solution has also been studied (Van Der Sluis *et al.* 1986).

In the case of Cu, Frost and Griffin (1977b) suggested that precipitation is the most important solution Cu control at pH levels greater than about 6.5. The most commonly identified solids incorporating Cu(II) include oxides (CuO), sulphates ($Cu_3SO_4(OH)_4$) and carbonates ($Cu_2(OH)_2CO_3$) depending on solution composition and $CO_2(g)$ partial pressure (Eary *et al.* 1990). Under oxidising conditions CuO would be the solubility controlling solid at pH values greater than 6 according to thermodynamics (Rai *et al.* 1987a). However, the precipitation of $Cu(OH)_2$ and

$Cu_2(OH)_2CO_3$ was implicated in one study of alkaline soils (Dhillon *et al.* 1981). Copper hydroxy sulphate has been found to be too soluble to limit concentrations in the acidic pH range and therefore adsorption/desorption mechanisms are likely to be the principle controls on aqueous Cu activity in acidic weathering environments (Rai *et al.* 1987a).

No well-defined solubility controlling solid for Zn has been reported in natural soils and sediments (Rai *et al.* 1984). Some experimental work has suggested that $ZnCO_3$ or $Zn(OH)_2$ may be a potential solubility controlling solid at high pH and Zn concentration (Singh and Sekhon 1977). In slightly acidic to alkaline conditions the concentration of Zn should be limited by $ZnO/Zn_5(OH)_6(CO_3)_2$ (Eary *et al.* 1990). Unpublished data of Rai (1984) as cited by Eary *et al.* (1990) showed that dissolved Cu and Zn concentrations from four different fly ash suspensions were consistent with the solubilities of CuO and ZnO respectively under near neutral to alkaline conditions.

Another potential control on ion activities is chemisorption which can produce solubilities for Cd^{2+} much lower than the solubility product predicted by $CdCO_3$ (McBride 1980; Papadopoulos and Rowell 1988). The observed affinity of calcite for metal ions seems to be a function of ionic radius with divalent metal ions of the same size as Ca^{2+} readily substituting for Ca^{2+} on accessible surface sites. Divalent Ca and Cd are close in ionic radius at 0.099 nm and 0.097 nm respectively however Zn^{2+} and Cu^{2+} are somewhat lower at 0.074 nm for Zn and 0.072 nm for Cu (Weast *et al.* 1983). However, Zn can specifically adsorb to calcite at Zn concentrations below those required for the precipitation of Zn compounds (Brummer *et al.* 1983). This process may be important in the phosphogypsum-soil mixes and in the soil alone treatments in this study.

Although not established in this study, the adsorption of Cd, Cu, and Zn could have occurred in the systems examined by complexation on organic matter, specific adsorption and ion exchange (Rai *et al.* 1984). Specific adsorption of Cd onto $CaCO_3$ (McBride 1980) and onto hydrous oxides of Fe, Al, Si and Mn (Kinniburg *et al.* 1977; Forbes *et al.* 1976; Benjamin and Leckie 1981) can occur and may be an important control on aqueous levels. Although both Cd^{2+} and Cu^{2+} decrease in adsorption in the presence of competing Ca^{2+} (Cavallaro and McBride 1978), Cd^{2+} appears to be selected over Ca^{2+} (Milberg *et al.* 1978). Divalent alkaline earths (Ca^{2+} and Mg^{2+}) also compete with Zn^{2+} for ion exchange sites (Shukla *et al.* 1980) and Zn^{2+} and Cd^{2+} compete for the same adsorption site on some minerals (Benjamin and Leckie 1980).

Adsorption of Cd, Cu and Zn is highly pH dependent, increasing with increasing pH (Farrah and Pickering 1977; Anderson and Christensen 1988). The pH dependence of Cd adsorption, for a number of materials, is influenced by the solution to solid ratio, the solution concentration of Cd, and the presence of competing cations or complexing ligands (Rai *et al.* 1987a). The degree of Cu adsorption is directly related to pH in the case of many metal oxides (McBride 1982; McKenzie 1980) and clay minerals (Frost and Griffin 1977b). Zinc has pH dependent adsorption on metal oxides (Benjamin and Leckie 1980) and soils. In the case of Cu, pH dependent adsorption is attributed to the adsorption of hydroxo complexes (ie $Cu(OH)^{+}$) which are more strongly held on the surface than the free ion (McKenzie 1980, Davis and Leckie 1978). The aqueous hydrolysis of Zn and the amphoteric nature of oxides and hydrous oxide minerals have been used to explain the pH dependence of Zn adsorption (Benjamin and Leckie 1980).

No solubility controlling solids were identified for Cd, Cu or Zn due to undersaturation of these elements relative to potential solubility controlling solids. The effects of precipitation/dissolution and adsorption/desorption could not be isolated in this case. However, the strong inverse relationships of Cd^{2+}, Cu^{2+}, and Zn^{2+} activities with pH indicate that the factors controlling aqueous levels in the systems under study limit the solution activities of these elements to a low level at neutral and higher pH levels.

ii. Selenium

Two Se diagrams were drawn, one using selenate (SeO_4^{2-}) which is the dominant Se ion in highly oxidised systems and one using hydrogen selenite ($HSeO_3^-$) which is the ion dominant in a less oxidised system in the acid to neutral pH range (Eary *et al.* 1990) (Fig. 41 and 42). Selenium was undersaturated relative to potential solubility controlling solids in both highly oxidised and less oxidised conditions. The distribution of sample points had no slope relative to pH. There was insufficient Se in the solid phase to bring Se to saturation relative to the potential solubility controlling solids examined.

Although solubility controlling solids for Se have been proposed (Elrashidi *et al.* 1987), in general selenate and selinite minerals are too soluble to act as solubility controls for Se under the oxidising conditions expected in most waste leaching environments (Rai *et al.* 1987a). Adsorption reactions are suggested as the primary controls on Se concentrations in these situations. In spite of their anionic nature SeO_4^{2-} and SeO_3^{2-} are adsorbed significantly in some soils (Rai *et al.* 1984).

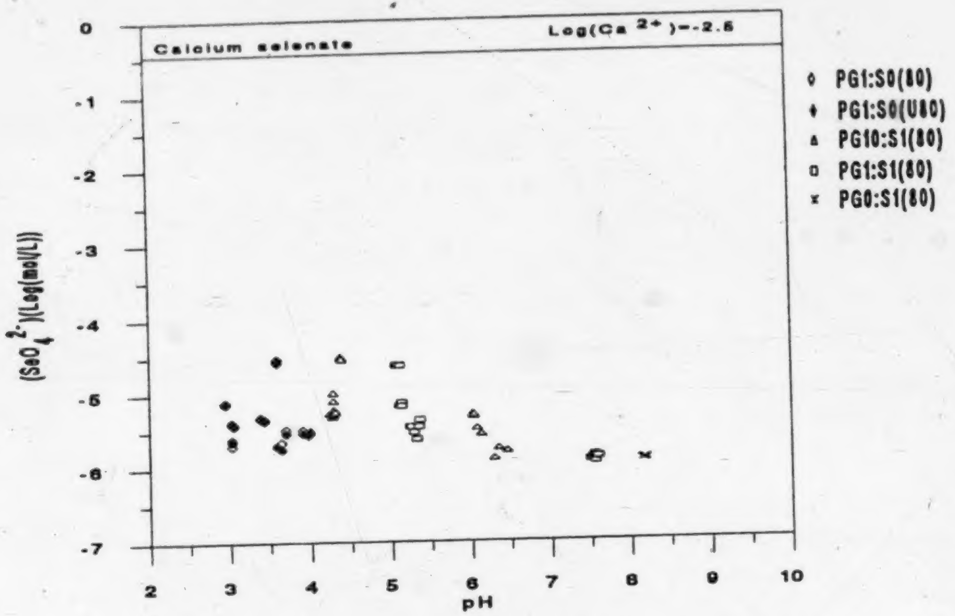

Figure 41. Calcium selenate solubility equilibrium with data from 80 day incubation.

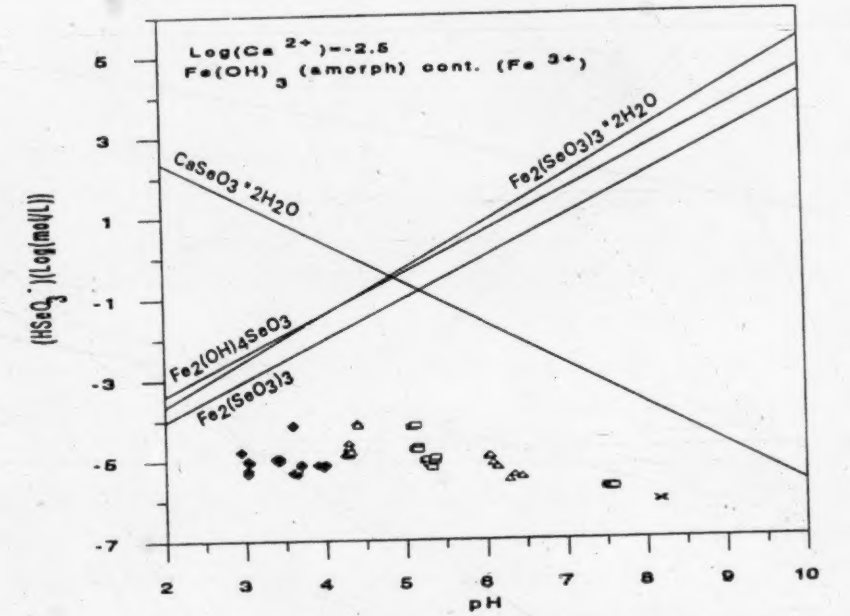

Figure 42. Solubility equilibria for some selenite minerals with data from 80 day incubation.

Thermodynamic data from Elrashidi et al. (1987), Lindsay (1979), and Rai et al. (1984).

However, SO_4^{2-} and PO_4^{3-} are able to compete with SeO_4^{2-} and SeO_3^{2-} for soil adsorption sites (Singh *et al.* 1981). Iron and Al oxides are the principle adsorbents in fossil fuel waste although adsorption of Se onto clays does occur (Frost and Griffin 1977a). There is indirect evidence for the irreversible adsorption of SeO_3^{2-} onto crystalline iron oxide surfaces (Hingston *et al.* 1974; Hamdy and Gissel-Nielson 1977) suggesting the formation of a solid phase. In some soils ferric oxide selenites could act as solubility controlling solids (Geering *et al.* 1968). Selenite and selenate are strongly adsorbed to goethite, amorphous iron hydroxide and gibbsite under acidic conditions but fractional adsorption decreases with increasing pH (Hingston *et al.* 1972; Leckie *et al.* 1980).

iii. Chromium

Chromium concentrations in leachates are expected to be limited by the solubility of Cr(III) solids (Rai *et al.* 1987b) including either $Cr(OH)_3$ or Cr(III) coprecipitated with Fe oxides and hydroxides. As in utility wastes, most of the Cr in the batch incubation extracts was expected to be present as Cr(III) and thus this form was used in the Cr solubility diagram (Fig. 43).

Chromium was undersaturated relative to the potential solubility controlling solids (Fig. 43). Above pH 4 most samples were at or near the detection limit and the slope observed above pH 4 was primarily a speciation effect. When pH increased from 3 to 4 there was a decrease in Cr concentration as well as a decrease in $Cr(OH)^{2+}$ activity with the activity decreasing by nearly 4 orders of magnitude indicating that a solubility controlling solid may have been having an effect. The distribution of points was similar in slope to the $Cr_xFe_{1-x}(OH)_3$ solid solution but the extracts were undersaturated relative to the modelled solid solution.

Calculations revealed that in phosphogypsum alone treatments, based on mean values of oven dried samples with detectable levels, there was 70 mg kg^{-1} Cr (only 2 samples were above the detection limit of 10 mg kg^{-1}) (Table 5). The maximum obtainable solution concentration for 300 g solid in 600 g water was in Log(mol L^{-1}) equal to -3. Thus in at least some of the samples there was sufficient Cr to bring the sample at or near saturation relative to $Cr_xFe_{1-x}(OH)_3$ if all of the phosphogypsum were to dissolve (Fig. 43). However, only a small portion of the matrix gypsum can dissolve to expose the surface of accessory minerals to the solution. A Cr proportion in the solid solution at much less than 0.1 would bring the isolines down further from $Cr_{0.1}Fe_{0.9}(OH)_3$ isoline but the Cr to Fe ratio in this material is approximately 0.2

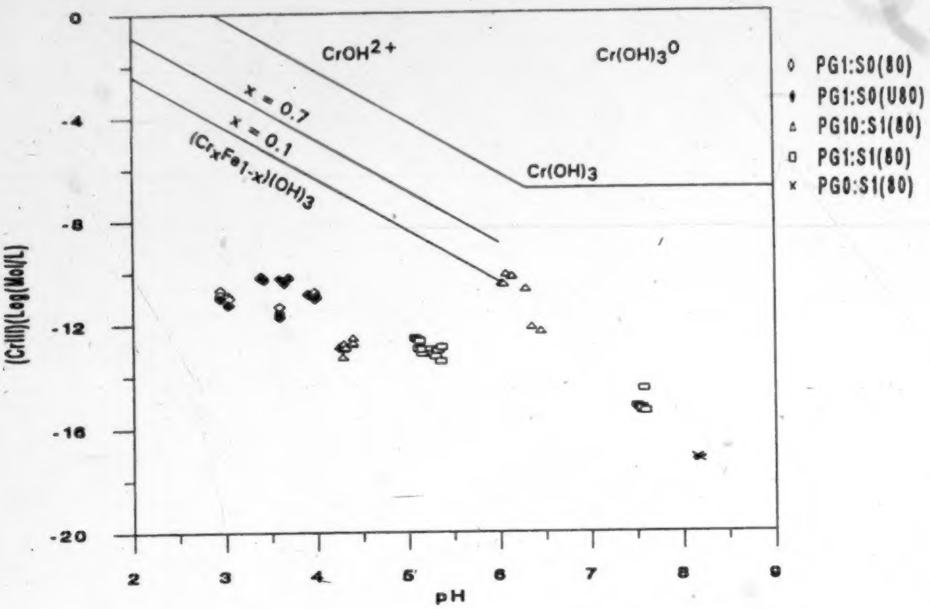

Figure 43. Solubility equilibria for some chromium minerals with data from 80 day incubation.

Thermodynamic data from Rai et al. (1984) and Rai et al. (1987a).

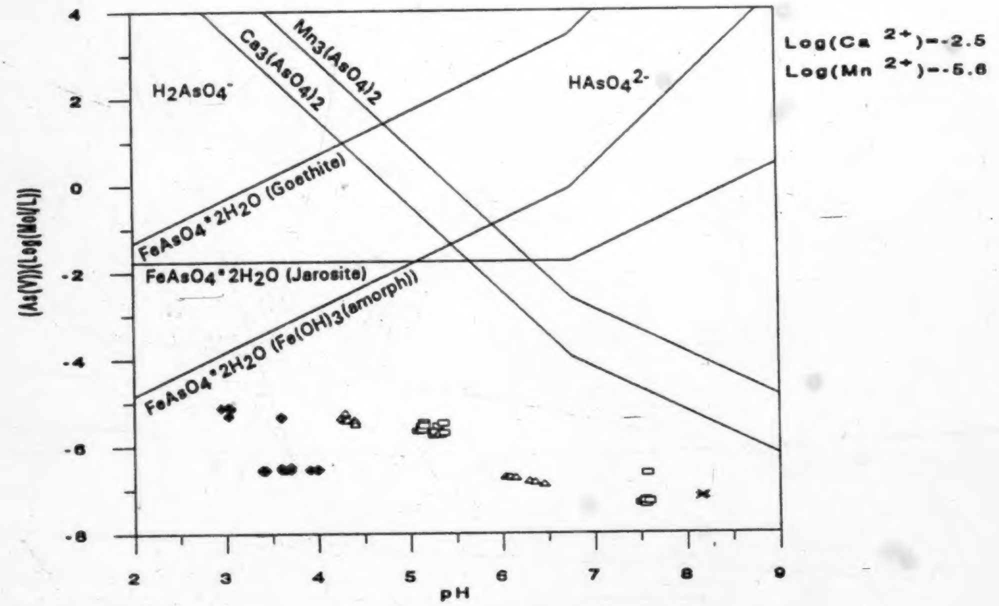

Figure 44. Solubility equilibria for some arsenic minerals with data from 80 day incubation.

Thermodynamic data from Dove and Rimstedt (1985), Hess and Blanchar (1976), Lindsay (1979), and Sadiq et al. (1983).

making moving the Cr proportion down by much more somewhat unrealistic.

Rai and Szelmeczka (1990) have reported the Cr concentrations in fly ash leachate amended with aqueous Cr(III) are consistent with the solubility of $Cr_xFe_{1-x}(OH)_3$. In their study, aqueous concentrations of Cr in the pH range most commonly encountered in environmental samples (5 to 10 (Baas Becking *et al.* 1960)) were at or near the detection limit leading the researchers to conclude that in general Cr is not expected to be significantly mobile. In neutral to alkaline solutions the solubility of $Cr(OH)_3$ is very low (near the detection limit of Cr) and thus $Cr(OH)_3$ can be used to set the upper limits on Cr concentrations for the mid-pH range (Rai *et al.* 1987a).

In most systems studied it is difficult to differentiate specific adsorption and the rapid formation of a solid solution of $Cr_xFe_{1-x}(OH)_3$ that has extremely low solubilities (Rai *et al.* 1987a). Chromium (III) is involved in adsorption reactions and like other hydrolyzable metals it shows an increase in adsorption with increasing pH (Griffin *et al.* 1977). However, adsorption can be an important mechanism at low pH (<4.5) and Cr concentration ($<10^{-6}$M) (Rai *et al.* 1984). Chromium strongly adsorbs to Fe and Mn oxides (Korte *et al.* 1976), and at higher concentrations it may undergo exchange reactions with layer lattice silicates (Griffin *et al.* 1977). Some organic materials can bind Cr under conditions prevalent in sea water (Nakayama *et al.* 1981).

With Cr, as with many of the other trace elements, many of the thermodynamic constants in the literature including those adopted in this study have had limited applicability and more research and updating has been and will continue to be required. For example, Rai *et al.* (1987b) noted that the hydrolysis constants for Cr(III) reported in the literature, particularly those for polynuclear species, were in error.

iv. Arsenic

Arsenate ions (AsO_4^{3-}) are predicted to be the dominant form of dissolved As in oxygenated solutions (Rai *et al.* 1987a). Arsenate ions, $H_2AsO_4^{2-}$ and $HAsO_4^-$, were used to develop the solubility equilibria diagram (Fig. 44) as they are the dominant arsenic species in the pH range of interest (Eary *et al.* 1990). They were undersaturated relative to potential solubility controlling solids showing little direct response to pH. Above a pH level of 6 the samples were at or near the detection limit for As. There was insufficient As in the solid phase to bring As to saturation relative to the potential solubility controlling solids examined.

The Ba levels in the sample extracts were too low for barium arsenate ($Ba_3(AsO_4)_2$) to be a potential solubility controlling solid although it has been suggested as the solid most likely to control As(V) in soil oxidising environments (Wagemann 1978). Another study suggested that scorodite ($FeAsO_4 {*} 2H_2O$) controls the AsO_4^{3-} levels in waters draining from oxidising arsenic-rich ores (Dove and Rimstedt 1985). Sadiq *et al.* (1983) postulated that $Ca_3(AsO_4)_2$ and/or $Mn_3(AsO_4)_2$ should limit As(V) concentrations in oxidising alkaline systems. In addition, Krauskopf (1955) noted that isomorphous substitution of AsO_4^{3-} for PO_4^{3-} may occur and so As(V)-enriched Ca phosphate minerals originating from As substituted phosphate rock, may serve as a solubility controlling solid for As in phosphogypsum.

In a study by Livesey and Huang (1981) soil solution AsO_4^{3-} levels fell below saturation limits for all arsenates and it was concluded that adsorption not precipitation was controlling AsO_4^{3-} levels in soils. Wangen and Jones (1984) found that As was effectively removed from acidic solutions through adsorption onto soil minerals which indicated that As oxyanions are naturally retained in the presence of oxide and clay minerals at a low pH. Arsenate ions have been observed to be most strongly adsorbed at a low pH with adsorption decreasing substantially over the pH range from 7 to 9 (Leckie *et al.* 1980). Studies have shown that adsorption of As(V) as AsO_4^{3-} is comparable to PO_4^{3-} and that it is strongly adsorbed in most soils and sediments (Wauchope 1975; Holm *et al.* 1979); PO_4^{3-} was found to substantially supress AsO_4^{3-} adsorption in some soils (Livesey and Huang 1981).

CHAPTER V

SUMMARY AND CONCLUSIONS

This study was designed to characterize the mineralogy and chemistry of gypsum based by-products of phosphate fertilizer production from a decommissioned plant site in Medicine Hat, Alberta. These by-products, termed phosphogypsum in the fertilizer industry, are generated through the wet process phosphoric acid production in which phosphate rock is acidulated with sulphuric acid producing phosphoric acid, gypsum and hydrofluoric acid. At most plant sites worldwide, the gypsum product generated as well as much of the fluoride wastes and various wastes from other process streams at the plant are sluiced to a permanent tailings pond or stack. There are a number of potential uses for phosphogypsum, however, they are not widely adopted due to economic and environmental constraints (Collings, 1980; Berish 1990).

The primary focus of this study was to identify directly and/or predict indirectly the potential solubility controlling solids for major and trace elements in phosphogypsum and in phosphogypsum-soil mixes. Solubility controlling solids if identified can aid in the prediction of the maximum attainable elemental concentrations in pore water (Mattigod *et al.* 1990) and thus are important in the assessment of the safety of inorganic waste disposal and utilisation.

The pH of the phosphogypsum samples collected ranged from 2.6 to 4.0, with the acidic nature being attributed to residual phosphoric acid which condensed on crystal surfaces as the material dried as well as to fluid inclusions within the gypsum crystals. Cation exchange capacity (CEC) was less than 10 cmol (+) kg^{-1}. Carbonate C was not detectable; however organic C ranged from 0.08 to 1.23 percent with samples of a darker color containing the highest levels. All of the dark color disappeared with heating to 450°C. Extractable NH_4^+-N and NO_3^--N ranged from 7.00 to 1260 and from 0.56 to 266 mg kg^{-1} oven dry solid respectively. The upper limit was an order of magnitude higher in NH_4^+-N and several times higher in NO_3^--N than a typical cultivated Alberta surface horizon (Malhi *et al.* 1985).

Phosphogypsum saturated paste extract chemistry was dominated by Ca followed by Na, K and Mg. Metal concentrations varied widely among samples with the coefficient of variation at over 80 percent in the case of K. The high variability was attributed to a failure to establish equilibrium conditions, to variable ionic strength evidenced by the electrical conductivity levels which would be strongly affected by levels of major anions such as F^-, PO_4^{3-} andSO_4^{2-}, and to variable pH. Base titration curves for pastes and extracts demonstrated that the samples were clustered into two groups. Samples 1, 4, and 6 showed limited buffering and had pH levels near 4 while samples 2, 3, 5, 7, and 8 were more highly buffered with pH levels near 3. The differences between the two groups were attributed to a higher level of condensed acid present in the latter group as compared with the former. Buffering occurred in the pH range from 6 to 8 indicating the presence of phosphoric acid.

The sand and till samples had pH levels between 7.5 and 8.5 and CEC levels of 5.7 and 11 cmol (+) kg^{-1} respectively. Extractable NH_4^+-N was 2.66 mg kg^{-1} for the sand and 3.22 mg kg^{-1} for the till, while the extractable NO_3^--N was 0.98 mg kg^{-1} for the sand and 5.46 mg kg^{-1} for the till. Organic C levels were near 0.50% in each sample and carbonate C was 0.55% in the sand and 1.01% in the till. Saturated paste extracts from the soils were dominated by Ca with the till releasing more of each element than the sand. The till extract had an electrical conductivity greater than the phosphogypsum extracts while that of the sand was lower.

Mineralogically, the phosphogypsum was comprised of gypsum with trace levels of quartz, sodium feldspar and residual phosphate rock. Samples were up to 10% SiO_2 and 1.6% P_2O_5. The gypsum matrix was made of well-defined crystals of tabular, tubular and needlelike morphology. Observed crystals fell within the silt size range.

The sand and till samples contained 1.5 and 14% clay respectively. Clay mineralogical analysis revealed that it was composed primarily of montmorillonite, kaolinite and mica in decreasing order of abundance.

The phosphogypsum samples were enriched, relative to shale, in the major elements of Ca, P, and S. Fluorine is also known to be elevated in the material (Kouloheris 1980, May and Sweeney 1980). For the trace elements, the phosphogypsum samples were elevated in Ag, Cd and Se by greater than 2 orders of magnitude over shale in some samples. Samples were also slightly enriched in Au, Sr and U. The relative distribution of the rare earth elements (REE) and Y followed closely the trends in marine phosphorite (Fleischer and Altschuler 1969). Yttrium and La were slightly elevated relative to shale whereas Ce was depleted and a number of the heavy REE showed comparable levels to shale.

The level of ^{226}Ra was greatest in the less aged, more acidic, buffered samples which also showed relative enrichment in organic C, cation exchange capacity and a number of trace and major elements. Most samples showed no detectable change in ^{226}Ra level through the extractions performed, supporting research suggesting that ^{226}Ra should be highly immobile in this system (May and Sweeney 1984; SENES, 1987). Radium levels in samples from the Medicine Hat stack have been measured to be 0.5 Bq g^{-1} (Roberts Thorne 1990) with the degree of enrichment ranging anywhere from 14 to 27 times over a typical soil (Roessler 1990).

From the time trial, it was evident that most ion activities approached stable levels in the pore water within 28 days. Activities of some ions including Ca^{2+}, SO_4^{2-}, and $H_2SiO_4^{2-}$, elemental concentrations, ion activity product corresponding to gypsum, and computer modelled ionic strength did not stabilise over the 90-day incubation. This was related to the formation of a freezing-induced gypsum precipitate during storage which did not redissolve with thawing. The degree of freezing-induced precipitation and dissolution with thawing could not be controlled among samples leading to erratic fluctuations in some chemical parameters. Elemental concentrations that were found to be significantly affected by freezing in the PG1:S0 treatment were Al, Ca, Fe, P, S, Se, Si, Sr, and Ti. Most erratic fluctuations of elemental concentrations were eliminated when they were converted to activities. This method of sample preservation can severely affect elemental levels in phosphogypsum extracts and thus it can not be recommended for this type of sample.

The distribution of pH values with time showed an apparent pattern, decreasing over the first 2 weeks and stabilising in the PG1:S0 and the PG10:S1 treatments. A slight inverse pH pattern was observed in the mined gypsum incubation. Activities of Al^{3+}, Cd^{2+}, Cu^{2+}, Fe^{3+}, $H_2PO_4^-$, $H_2SiO_4^{2-}$ and Zn^{2+} seemed to follow inverse trends with pH. Speciation effects as controlled by pH appeared to govern the activities of $HAsO_4^{2-}$ and $H_2AsO_4^-$, $Cr(OH)_2^+$, $Cr(OH)_3^0$, $HSeO_3^-$ and the SeO_4^{2-} over time as their corresponding elemental concentrations changed very little in most treatments particularly when the effects of dilution of the phosphogypsum with soil mixing were considered. Ionic strength calculated from electrical conductivity showed a slight inverse trend relative to pH while ionic strength generated by GEOCHEM from input elemental concentrations demonstrated only comparable erratic patterns to those of Ca^{2+} and SO_4^{2-} activities.

Concentrations of Cd, Se, SO_4^{2-}-S and total dissolved solids (TDS) exceeded Canadian drinking water standards (DWS) in all of the pore water samples from PG1:S0. In some samples, levels of As, Cr, Cu, Fe, Mn, Na, NO_3^--N, and Zn exceeded DWS. Values for pH were outside the acceptable range for DWS. With soil mixing, most elemental concentrations decreased to near DWS as most elements were at or near the detection limit. However, for a number of sample extracts, As, Cd, Cu, Se, Mn, Na, NO_3^--N, SO_4^{2-}-S, Zn, and TDS remained in excess of DWS in extracts from the phosphogypsum-soil mixes. In the soil alone, only Na, SO_4^{2-}-S and TDS were in excess of DWS. Notably, small decreases in the amount of As, NO_3^--N, and

Se with soil additions could not be attributed to more than the effect of the dilution of the phosphogypsum with soil mixing.

Potential solubility controlling solids were predicted for all of the major elements examined using solubility equilibria diagrams, however, all of the trace elements were undersaturated relative to identified solubility controlling solids. For Ca, gypsum was assigned in the acidic to neutral systems transferring to calcite under alkaline systems. Sulphate levels were also predicted to be controlled by gypsum. Phosphorus levels appeared to be controlled by fluorapatite in the phosphogypsum alone system and by hydroxyapatite and/or ß-tricalcium phosphate when mixed with soil. Other calcium phosphate minerals may coexist in systems with pH levels in the near neutral range. Predicted solubility controlling solids for Al included alunite, basaluminite, gibbsite, and jurbanite, and for Fe, amorphous $Fe(OH)_3$, goethite, and jarosite. For Si, amorphous silica could be used to estimate maximum attainable Si concentrations in the systems under study as all samples were undersaturated relative to this mineral.

Activities of Cd^{2+}, Cu^{2+} and Zn^{2+} followed strong inverse trends with pH but were undersaturated relative to potential solubility controlling solids and there was insufficient amount of each element in the system to come to saturation. Therefore, it was impossible to predict the equilibria isolines for potential solubility controlling solids. The effect of precipitation/dissolution and adsorption/desorption could not be differentiated as in both cases an inverse relationship between cation activity and pH can occur (Lindsay 1979; McKenzie 1980; Frost and Griffin 1977b). Similarly solubility controlling solids for As, Cr and Se could not be predicted due to undersaturation, with As and Se being present in the solid at levels too low to bring them to saturation relative to potential solubility controlling solids. A spiking experiment, in which equilibrium is approached from oversaturation, as those designed by Rai and Szelmeczka (1990) in which they focused on Cr in fly ash, would help to elucidate the presence or absence of trace element solubility controlling solids.

Solubility controlling solids could not be predicted for the trace elements examined due to insufficient quantities present producing undersaturation relative to the potential minerals for which thermodynamic data were available. However, the strong inverse trends of Cd^{2+}, Cu^{2+} and Zn^{2+} activities relative to pH demonstrated that as phosphogypsum or phosphogypsum pore water is neutralised by aging or by mixing with subsurface carbonate rich geological material or groundwater, the pore water concentrations of these elements decrease substantially to at or near background levels. Chromium concentrations demonstrated some of the same inverse trends. However, As, NO_3^--N, Se, and SO_4^{2-}-S concentrations did not decrease significantly as pH increased. Furthermore the behaviour of F, an element enriched in phosphogypsum, was not examined in this study. Leaching of one or more of these elements into the carbonate rich parent geological material below the stack at Medicine Hat may elevate normal background levels.

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APPENDIX I

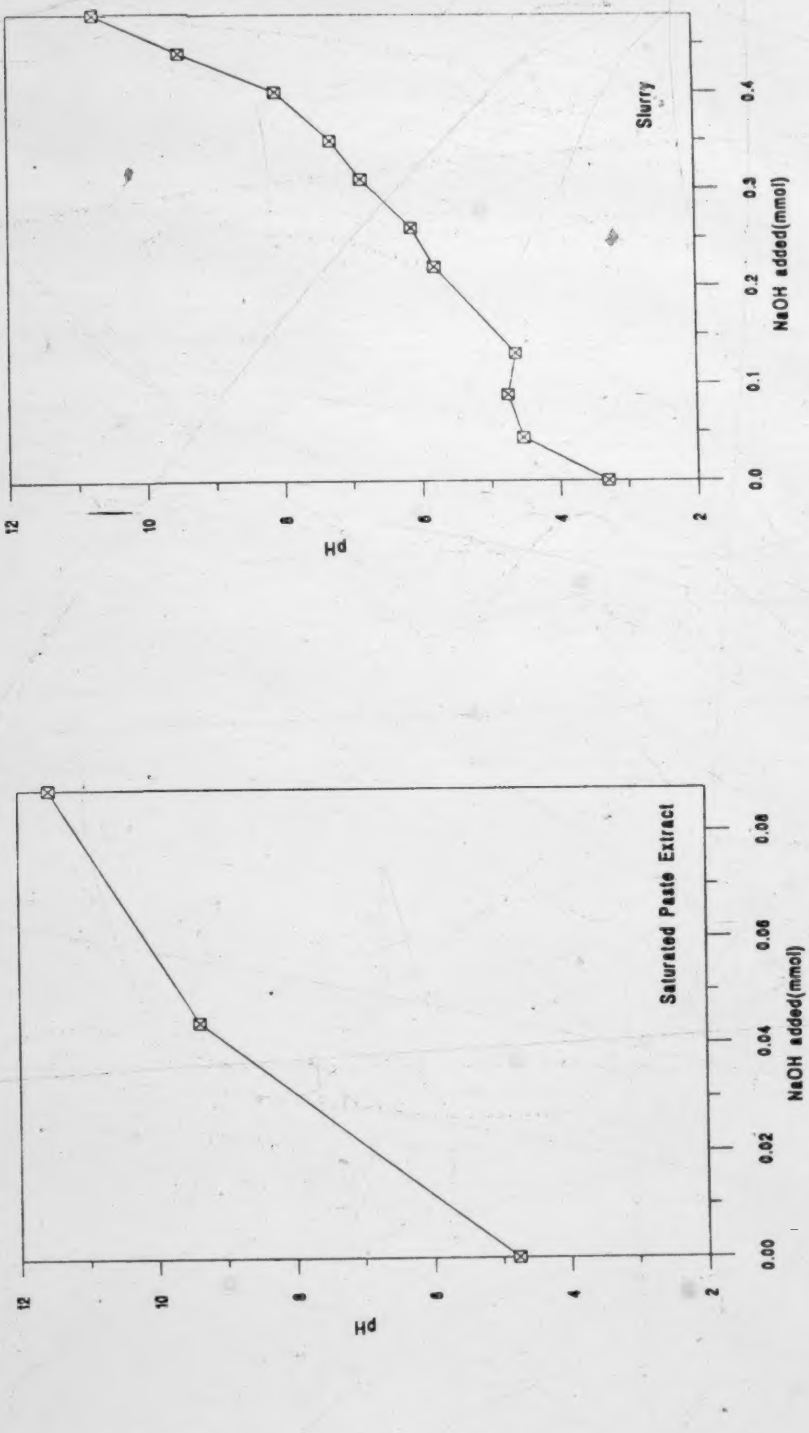

Figure 1. Base titration of phosphogypsum sample 1.

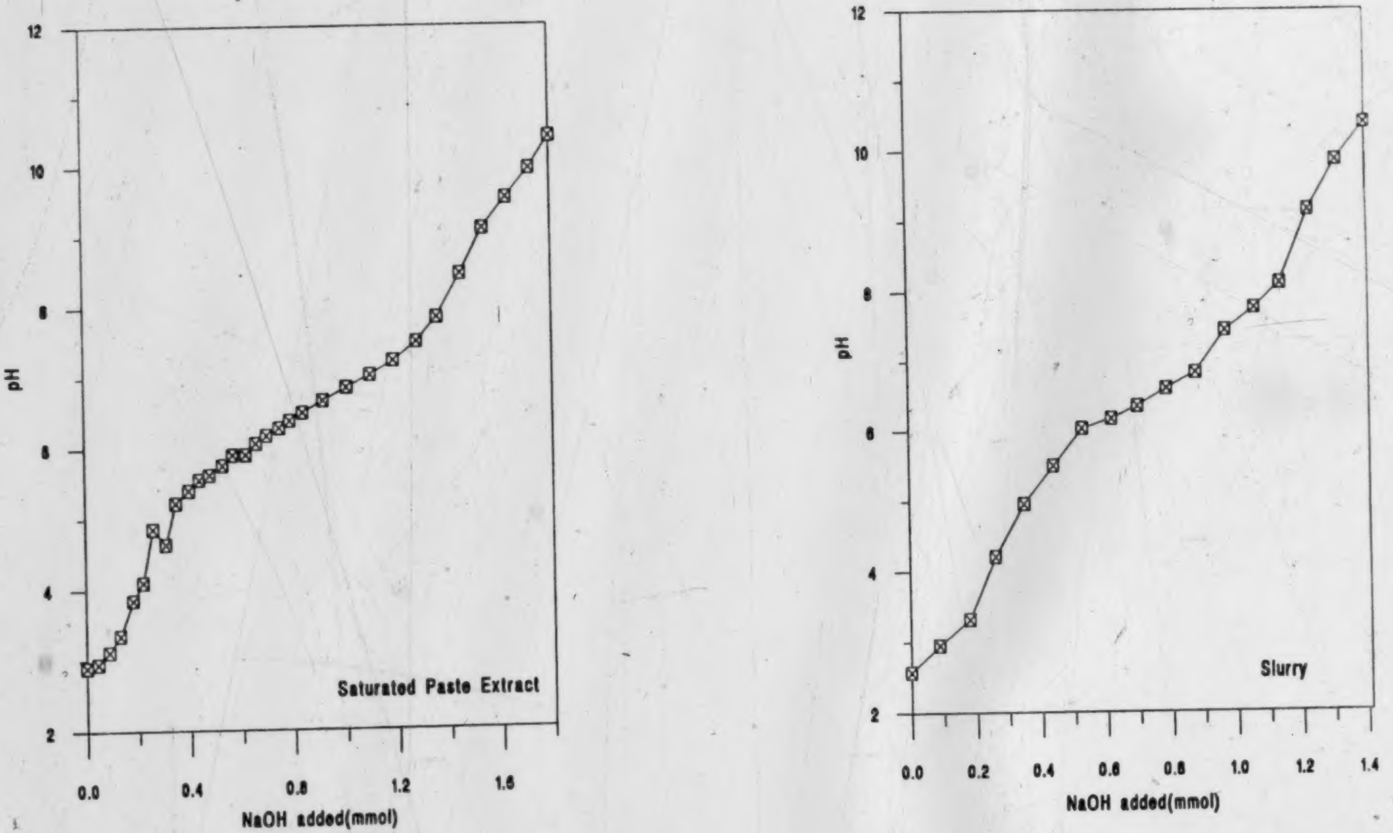

Figure 2. Base titration of phosphogypsum sample 2.

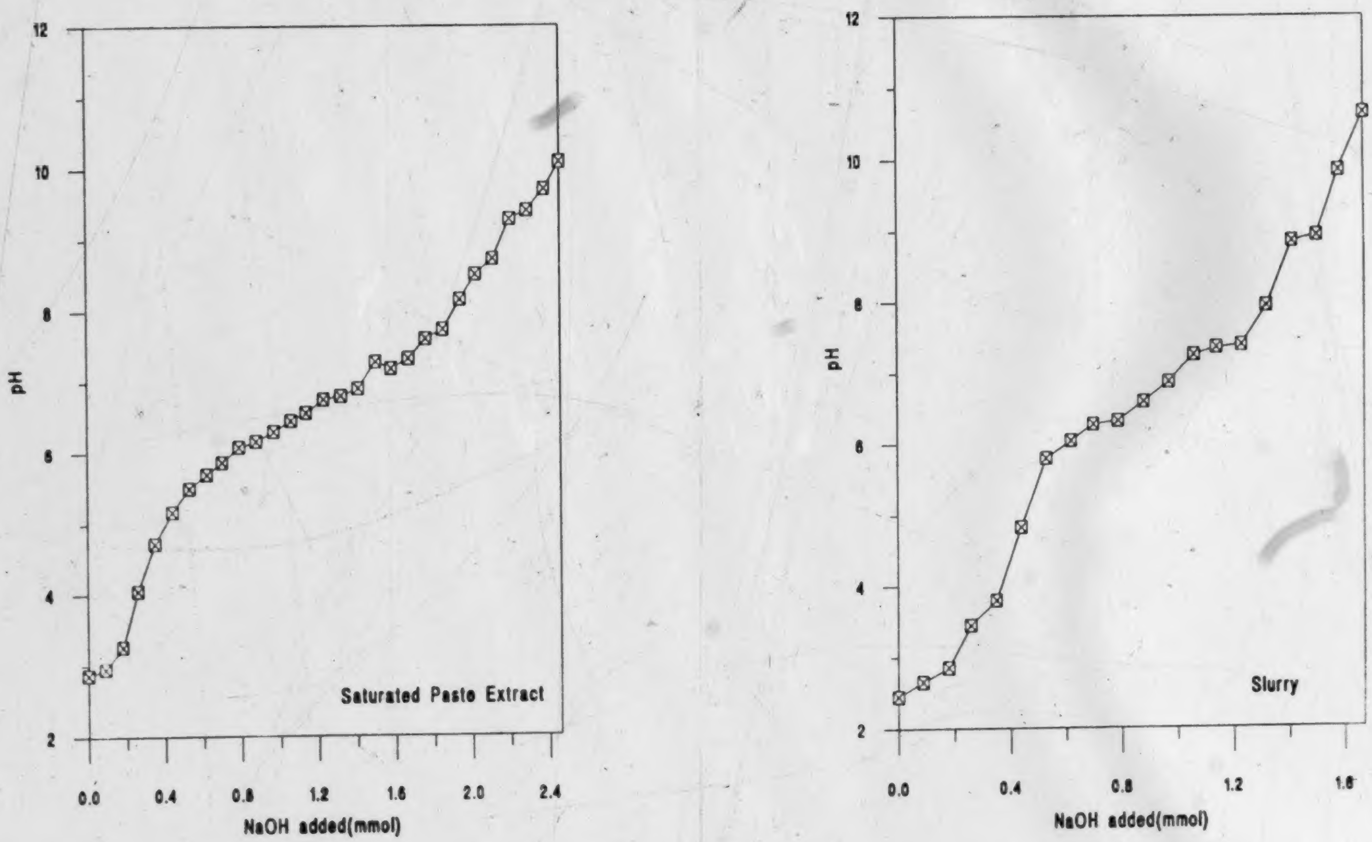

Figure 3. Base titration of phosphogypsum sample 3.

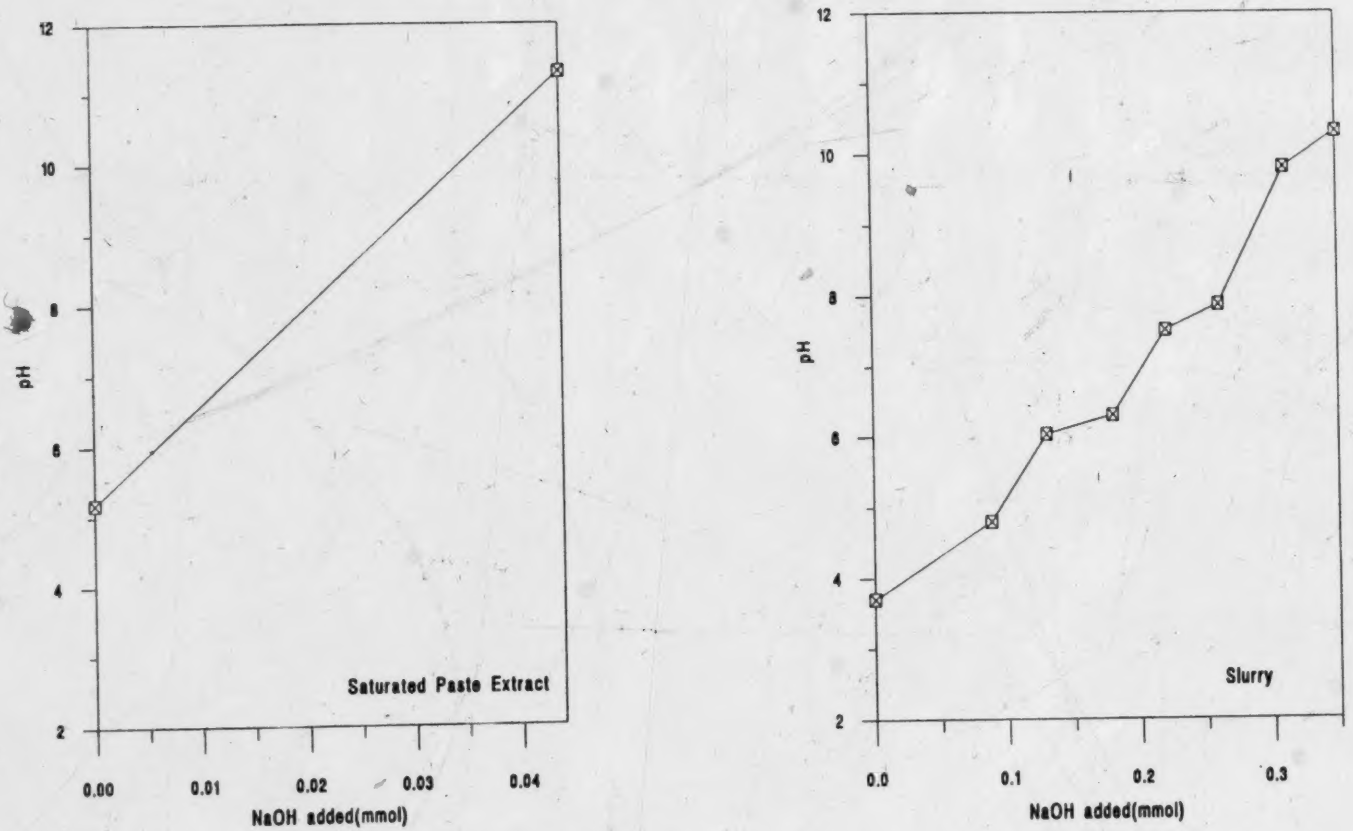

Figure 4. Base titration of phosphogypsum sample 4.

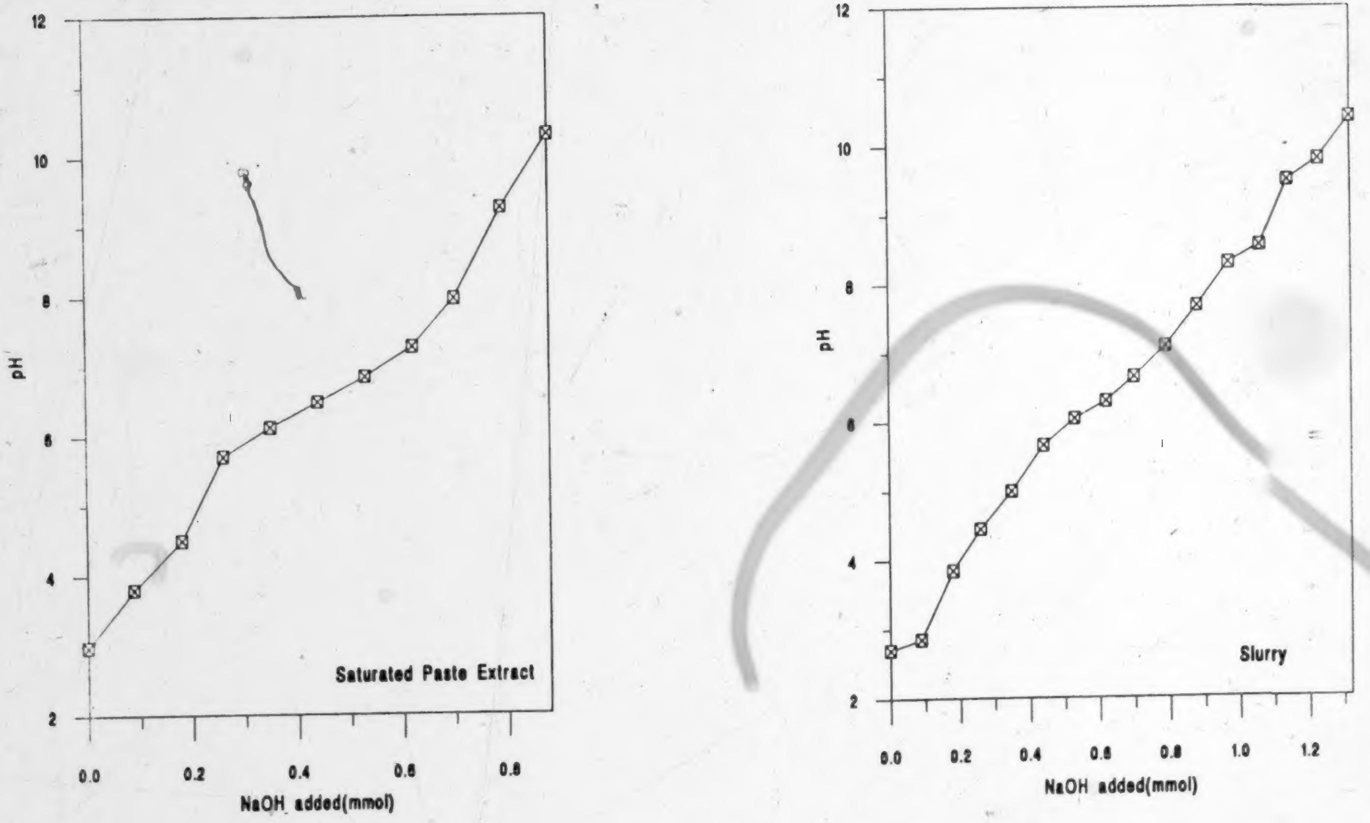

Figure 5. Base titration of phosphogypsum sample 7.

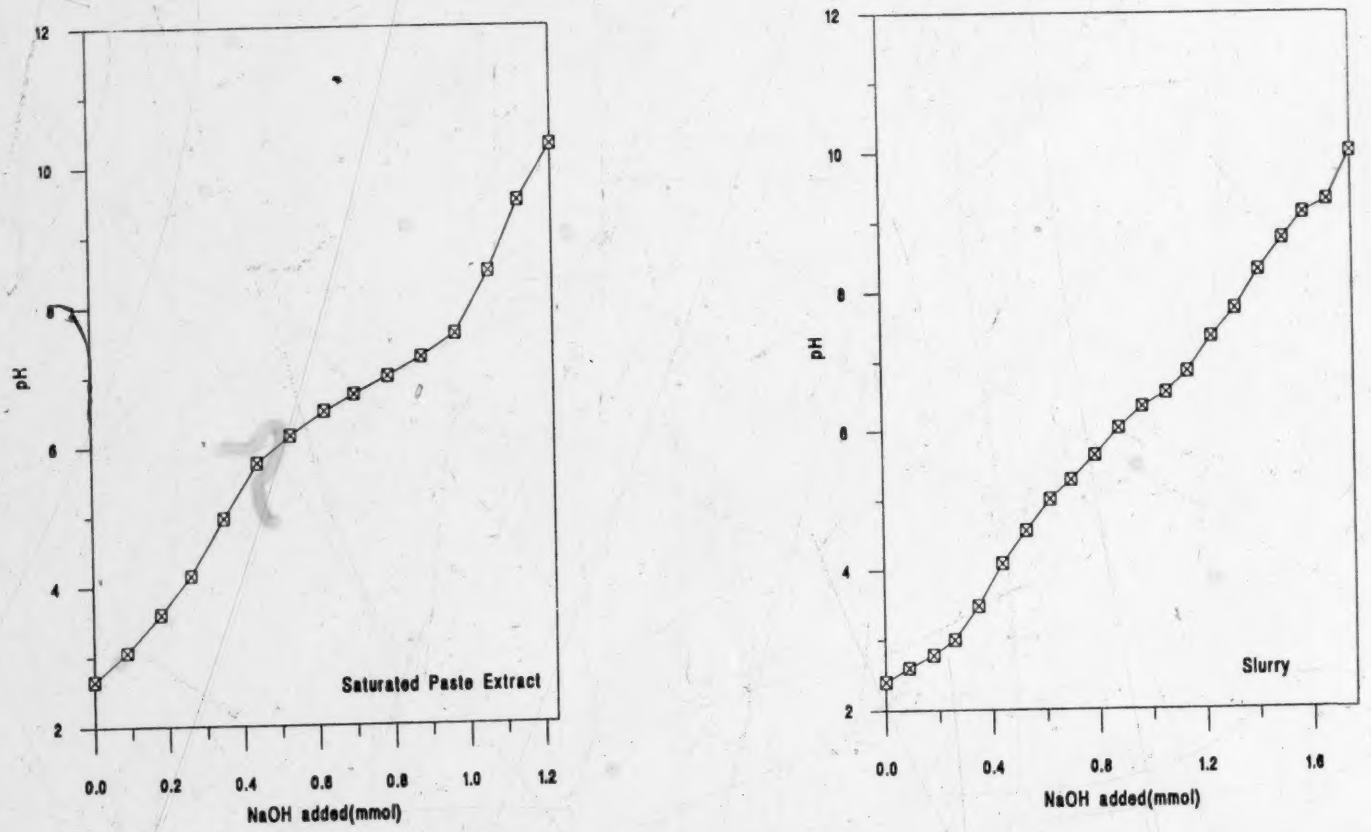

Figure 6. Base titration of phosphogypsum sample 8.

APPENDIX II

Table 1. Pore water chemical analyses from the time trial PG1:S0 treatment (mg/L).

Param.	DL^z	Time of Sampling (days) and Replicate Number																				
		1r1	1r2	1r3	7r1	7r2	7r3	14r1	14r2	14r3	28r1	28r2	28r3	60r1	60r2	60r3	80r1	80r2	80r3	90r1	90r2	90r3
Al	0.2	5.5	6.3	5.8	10	9.7	10	13	12	13	14	14	13	10	11	12	17	14	15	11	12	13
As	0.03	‡	‡	‡	‡	‡	‡	‡	‡	‡	‡	‡	‡	‡	‡	‡	‡	‡	‡	‡	‡	‡
B	0.04	‡	‡	‡	‡	‡	‡	‡	‡	‡	‡	‡	‡	‡	‡	‡	‡	‡	‡	‡	‡	‡
Ba	0.005	0.020	0.024	0.024	0.031	0.036	0.040	0.032	0.033	0.037	0.027	0.023	0.029	0.028	0.020	0.017	0.025	0.026	0.017	0.019	0.017	0.017
Ca	0.05	476.10	488.70	475.40	597.00	430.50	453.60	504.70	497.30	520.10	483.50	458.50	385.20	263.20	286.70	263.40	632.30	416.40	380.30	280.20	329.20	308.50
Cd	0.01	0.18	0.21	0.20	0.31	0.31	0.33	0.41	0.39	0.42	0.47	0.47	0.47	0.38	0.43	0.46	0.57	0.53	0.54	0.43	0.44	0.51
Co	0.01	‡	‡	‡	‡	‡	‡	‡	‡	‡	‡	‡	‡	‡	‡	‡	‡	‡	‡	‡	‡	‡
CO_3^{2-}-C^y	§	2.16	1.85	1.85	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Cr	0.02	‡	‡	‡	‡	‡	‡	0.03	0.03	0.03	0.05	0.04	0.05	0.04	0.03	0.04	0.04	0.03	0.03	0.02	‡	0.03
Cu	0.01	0.25	0.34	0.29	0.76	0.78	0.78	1.11	1.06	1.08	1.07	1.07	1.05	0.77	0.87	0.89	1.10	0.99	1.00	0.79	0.81	0.90
Fe	0.01	‡	‡	‡	0.03	0.04	0.04	0.04	0.05	0.03	0.03	0.02	0.04	0.04	0.02	0.02	0.02	0.02	0.02	0.01	0.02	0.02
K	0.2	1.6	1.6	2.3	0.9	1.6	1.7	1.6	1.7	2.0	2.2	2.2	2.6	3.1	2.8	3.1	3.1	3.1	3.2	3.1	3.1	3.2
Li	0.04	‡	‡	‡	‡	‡	‡	‡	‡	‡	‡	‡	‡	‡	‡	‡	‡	‡	‡	‡	‡	‡
Mg	0.1	0.4	0.3	0.4	0.1	0.3	0.3	0.3	0.3	0.3	0.4	0.4	0.5	0.5	0.4	0.5	0.8	0.5	0.5	0.5	0.4	0.6
Mn	0.006	0.025	0.028	0.025	0.029	0.028	0.030	0.037	0.035	0.037	0.042	0.041	0.042	0.045	0.046	0.048	0.064	0.057	0.058	0.049	0.048	0.058
Mo	0.05	‡	‡	‡	‡	‡	‡	‡	‡	‡	‡	‡	‡	‡	‡	‡	‡	‡	‡	‡	‡	‡
Na	0.05	1.70	1.79	1.94	2.17	2.26	2.45	2.97	2.93	3.25	3.85	3.88	4.24	4.40	4.35	4.80	5.69	5.33	5.66	4.88	4.99	5.57
NH_4^+-N	§	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.50	1.55	1.78	1.50	1.50	1.75
NO_3^--N	§	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.15	0.13	0.18	0.14	0.13	0.15
Ni	0.03	‡	‡	‡	‡	‡	‡	‡	‡	‡	‡	‡	‡	0.05	0.04	0.04	0.05	0.05	0.04	0.04	0.04	0.05
P	0.1	21.0	25.8	23.5	42.6	40.1	42.2	61.3	58.6	61.5	78.3	79.1	78.6	72.6	78.5	83.0	115	103	108	86.0	90.6	99.8
Pb	0.1	‡	‡	‡	‡	‡	‡	‡	‡	‡	‡	‡	‡	‡	‡	‡	‡	‡	‡	‡	‡	‡
S	0.1	364.0	372.0	361.2	449.1	325.4	341.8	376.3	371.0	387.4	349.9	332.2	273.3	180.2	195.1	177.3	445.2	285.8	255.5	186.8	223.2	204.1
Se	0.3	‡	‡	‡	‡	‡	‡	‡	0.4	0.4	0.4	0.5	0.5	0.6	0.6	0.6	0.7	0.8	0.6	0.6	0.6	0.7
Si	0.1	0.8	0.9	1.0	1.8	1.6	1.6	2.2	2.1	2.3	2.4	2.3	2.3	1.9	2.0	2.1	3.6	2.9	3.1	2.1	2.4	2.5
Sr	0.009	2.642	3.034	2.711	5.139	4.131	4.375	5.876	5.773	6.002	6.717	6.651	6.118	4.452	4.964	4.689	8.963	7.150	7.064	5.181	5.856	5.848
Tl	0.01	0.02	0.03	0.03	0.01	0.02	0.02	0.02	0.02	0.03	0.02	0.02	0.02	0.03	0.02	0.02	0.03	0.03	0.02	0.02	0.02	0.02
V	0.03	0.17	0.18	0.18	0.10	0.11	0.12	0.16	0.16	0.18	0.15	0.15	0.16	0.12	0.13	0.14	0.15	0.14	0.14	0.12	0.12	0.14
Zn	0.02	0.48	0.52	0.53	0.86	0.78	0.83	0.97	0.97	1.08	1.05	1.11	1.16	0.83	0.95	1.07	1.29	1.15	1.26	0.90	0.95	1.15
pH(U)^x	§	5.1	5.1	4.8	4.2	4.1	4.1	3.8	3.8	3.7	3.9	3.9	3.9	4.0	4.0	3.9	3.9	3.8	3.9	3.9	3.9	3.8
pH(F)^w	§	4.7	4.6	4.5	4.0	3.9	3.9	3.7	3.7	3.7	3.7	3.8	3.7	3.8	3.6	3.6	4.0	3.8	3.7	3.8	3.7	3.7
EC^v(U)	§	1.9	2.0	2.0	2.1	2.1	2.1	2.1	2.0	2.1	2.2	2.2	2.1	2.2	2.2	2.2	2.2	2.2	2.2	2.2	2.2	2.2
EC(F)	§	2.1	2.1	2.1	2.2	2.1	2.2	2.2	2.1	2.2	2.2	2.1	2.1	1.8	1.6	1.8	2.2	2.0	2.1	1.7	1.8	1.7
IS^u(U)	§	0.025	0.025	0.026	0.027	0.028	0.027	0.027	0.026	0.027	0.029	0.028	0.028	0.029	0.028	0.029	0.029	0.029	0.029	0.029	0.029	0.029
IS(F)	§	0.027	0.027	0.028	0.028	0.028	0.028	0.028	0.027	0.028	0.028	0.027	0.027	0.024	0.021	0.024	0.028	0.026	0.027	0.022	0.024	0.022
ISmod^t	§	0.033	0.034	0.033	0.040	0.031	0.032	0.036	0.035	0.036	0.034	0.033	0.028	0.020	0.022	0.020	0.043	0.030	0.028	0.021	0.024	0.023
ID^s	§	6.2	6.0	6.8	8.5	7.7	8.0	8.6	9.1	9.6	9.2	8.8	10	9.5	10	10	11	11	12	11	11	11

[z] denotes detection limit; [y] denotes alkalinity in mg/L C; [x] samples left unfrozen prior to analysis; [w] samples frozen prior to analysis; [v] electrical conductivity in dS/m; [u] ionic strength calculated from EC in mol/L; [t] ionic strength calculated using GEOCHEM; [s] ion difference in percentage of free cationic charge relative to total cationic charge; ‡ denotes content below detection limit; § denotes data unavailable.

Table 2. Pore water chemical analyses from the time trial PG10:S1 treatment (mg/L).

		Time of Sampling (days) and Replicate Number																				
Param.	DL^z	1r1	1r2	1r3	7r1	7r2	7r3	14r1	14r2	14r3	28r1	28r2	28r3	60r1	60r2	60r3	80r1	80r2	80r3	90r1	90r2	90r3
Al	0.2	2.0	2.0	1.9	1.6	2.1	1.9	1.8	1.7	1.5	1.5	1.7	1.7	1.3	1.3	1.1	1.3	1.3	1.5	1.4	1.3	1.3
As	0.03	╪	╪	╪	╪	╪	╪	╪	╪	╪	╪	╪	╪	╪	╪	╪	╪	╪	╪	╪	╪	╪
B	0.04	╪	╪	╪	╪	╪	╪	╪	╪	╪	╪	╪	╪	╪	╪	╪	╪	╪	╪	╪	╪	╪
Ba	0.005	╪	╪	╪	╪	╪	╪	╪	0.010	0.007	╪	╪	╪	╪	0.005	╪	0.005	0.006	0.007	0.007	0.006	0.007
Ca	0.05	470.90	478.70	463.50	383.70	481.20	442.90	425.70	349.0	331.90	342.40	381.40	370.30	294.10	274.60	236.60	279.30	285.10	317.80	303.90	283.50	260.90
Cd	0.01	╪	╪	╪	0.02	0.02	0.02	0.02	0.03	0.03	0.02	0.02	0.03	0.02	0.03	╪	0.02	0.02	0.02	0.03	0.03	0.03
Co	0.01	╪	╪	╪	╪	╪	╪	╪	╪	╪	╪	╪	╪	╪	╪	╪	╪	╪	╪	╪	╪	╪
CO_3^{2-}-C^y	§	3.71	4.94	4.63	3.09	3.46	3.09	3.09	2.47	2.78	2.47	2.66	2.78	2.16	2.16	2.47	2.78	2.78	2.53	2.66	2.78	2.47
Cr	0.02	╪	╪	╪	╪	╪	╪	╪	╪	╪	╪	╪	╪	╪	╪	╪	╪	╪	╪	╪	╪	╪
Cu	0.01	╪	╪	╪	╪	╪	╪	╪	╪	╪	╪	╪	╪	╪	╪	╪	╪	╪	╪	╪	╪	╪
Fe	0.01	╪	╪	╪	╪	╪	╪	╪	╪	╪	╪	╪	╪	╪	╪	╪	╪	╪	╪	╪	╪	╪
K	0.2	3.3	3.8	3.5	3.3	3.4	3.6	3.4	3.8	3.5	3.6	3.8	3.7	3.8	4.0	3.9	3.9	4.0	4.5	4.6	4.5	4.4
Li	0.04	╪	╪	╪	╪	╪	╪	╪	╪	╪	╪	╪	╪	╪	╪	╪	╪	╪	╪	╪	╪	╪
Mg	0.1	72.5	72.8	78.0	77.6	80.6	80.9	84.3	80.9	81.1	79.2	84.8	83.1	69.7	76.9	71.5	68.1	71.7	74.5	81.0	80.5	74.3
Mn	0.006	0.016	0.014	0.016	0.128	0.142	0.146	0.217	0.262	0.287	0.225	0.293	0.329	0.227	0.300	0.301	0.219	0.273	0.315	0.266	0.310	0.311
Mo	0.05	╪	╪	╪	╪	╪	╪	╪	╪	╪	╪	╪	╪	╪	╪	╪	╪	╪	╪	╪	╪	╪
Na	0.05	32.82	33.30	35.02	32.57	33.31	33.37	32.69	32.15	31.93	31.03	32.38	31.85	28.95	29.64	28.42	27.21	28.02	28.69	29.57	29.62	27.96
NH_4^+-N	§	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.22	0.14	0.25	0.10	0.12	0.11
NO_3^--N	§	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.71	0.30	0.21	0.81	0.30	0.23
Ni	0.03	╪	╪	╪	╪	╪	╪	╪	╪	╪	╪	╪	╪	╪	╪	╪	╪	╪	╪	╪	╪	╪
P	0.1	1.6	1.2	1.6	3.5	3.8	3.5	3.6	3.7	3.7	2.9	3.4	3.6	2.3	2.8	2.5	2.2	2.6	2.8	2.5	2.7	2.5
Pb	0.1	╪	╪	╪	╪	╪	╪	╪	╪	╪	╪	╪	╪	╪	╪	╪	╪	╪	╪	╪	╪	╪
S	0.1	475.9	484.6	480.0	418.3	495.8	467.5	458.4	394.2	380.4	387.2	425.9	414.4	336.3	331.4	295.0	322.6	332.5	360.7	359.6	343.3	317.6
Se	0.3	╪	╪	╪	╪	╪	╪	0.4	0.5	0.5	0.5	0.5	0.6	0.4	0.6	0.5	0.5	0.6	0.6	0.5	0.6	0.6
Si	0.1	6.9	6.4	7.6	5.6	7.9	6.7	6.1	4.6	4.1	4.5	4.8	4.6	4.2	3.5	2.8	4.4	3.9	3.7	5.1	4.1	2.8
Sr	0.009	1.959	1.958	1.881	1.997	2.390	2.224	2.417	2.050	1.963	2.189	2.439	2.335	2.046	1.934	1.728	2.051	2.055	2.275	2.214	2.069	1.922
Ti	0.01	0.02	╪	0.02	0.01	0.02	0.01	0.01	0.02	0.01	0.01	0.01	0.01	╪	0.01	╪	0.01	0.01	0.01	0.01	0.02	0.02
V	0.03	0.10	0.11	0.12	0.05	0.07	0.07	0.05	0.05	0.05	0.04	0.04	0.04	╪	0.04	0.03	╪	0.03	0.03	0.04	0.04	0.04
Zn	0.02	╪	╪	╪	0.08	0.02	╪	╪	╪	0.02	╪	╪	╪	╪	╪	╪	╪	╪	╪	╪	╪	╪
pH(U)^x	§	6.8	6.9	6.9	6.4	6.5	6.5	6.4	6.3	6.3	6.4	6.5	6.3	6.2	6.3	6.3	6.2	6.2	6.3	6.3	6.2	6.2
pH(F)^w	§	6.2	6.3	6.4	5.6	5.8	5.7	5.5	5.4	5.4	5.2	5.2	5.2	5.1	5.1	5.2	5.2	5.2	5.2	5.3	5.2	5.2
EC^v(U)	§	2.2	2.2	2.2	2.2	2.3	2.3	2.3	2.3	2.3	2.3	2.4	2.4	2.4	2.4	2.4	2.5	2.5	2.5	2.5	2.5	2.5
EC(F)	§	2.3	2.3	2.4	2.4	2.4	2.4	2.4	2.4	2.4	2.4	2.4	2.4	2.4	2.3	2.3	2.1	2.4	2.1	2.2	2.2	2.2
IS^u(U)	§	0.028	0.029	0.029	0.029	0.030	0.029	0.030	0.030	0.030	0.030	0.031	0.031	0.032	0.031	0.031	0.032	0.032	0.032	0.032	0.032	0.032
IS(F)	§	0.030	0.030	0.031	0.032	0.031	0.031	0.031	0.031	0.031	0.031	0.031	0.031	0.032	0.030	0.030	0.028	0.031	0.028	0.028	0.028	0.028
ISmod^t	§	0.042	0.042	0.042	0.037	0.044	0.041	0.040	0.036	0.034	0.035	0.038	0.037	0.031	0.030	0.028	0.030	0.031	0.033	0.033	0.032	0.029
ID^s	§	5.1	4.9	4.9	4.1	4.9	4.5	4.8	4.7	5.0	4.5	4.2	4.7	4.8	4.5	3.9	4.0	4.1	4.8	4.2	4.3	4.1

^{z} denotes detection limit; ^{y} denotes alkalinity in mg/L C; ^{x} samples left unfrozen prior to analysis; ^{w} samples frozen prior to analysis; ^{v} electrical conductivity in dS/m; ^{u} ionic strength calculated from EC in mol/L; ^{t} ionic strength calculated using GEOCHEM; ^{s} ion difference in percentage of free cationic charge relative to total cationic charge; ╪ denotes content below detection limit; § denotes data unavailable.

Table 3. Pore water chemical analyses from the time trial PG1:S1 treatment (mg/L).

Param.	DL^z	Time of Sampling (days) and Replicate Number 1r1	1r2	1r3	7r1	7r2	7r3	14r1	14r2	14r3	28r1	28r2	28r3	60r1	60r2	60r3	80r1	80r2	80r3	90r1	90r2	90r3
Al	0.2	1.2	1.2	1.1	1.4	1.4	1.1	1.4	1.2	1.1	1.4	1	0.8	0.5	0.5	0.7	0.9	0.7	0.9	0.5	0.9	0.6
As	0.03	0.03	0.03	ǂ	ǂ	ǂ	ǂ	0.03	0.03	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ
B	0.04	0.05	ǂ	0.04	0.05	0.04	0.06	0.06	0.07	0.05	0.06	0.06	0.05	0.07	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.05
Ba	0.005	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ
Ca	0.05	307.10	319.40	298.40	376.10	426.20	304.70	361.20	309.20	290.00	380.20	288.10	233.90	132.55	126.35	188.66	246.90	174.58	242.70	138.05	240.40	175.18
Cd	0.01	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ
Co	0.01	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ
CO$_3^{2-}$-C^y	§	16.7	13.9	13.0	§	17.0	14.5	15.1	13.6	12.4	11.4	11.1	10.5	8.65	8.65	8.65	9.26	7.41	8.34	7.72	7.60	8.03
Cr	0.02	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ
Cu	0.01	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ
Fe	0.01	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ
K	0.2	10	9.6	9.6	9.8	9.7	9.5	9.8	9.7	9.6	10	10	9.9	10	10	9.9	11	10	11	11	11	11
Li	0.04	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	0.04	0.04	ǂ	0.04	0.04	0.05	0.05	0.05	0.04	0.04	0.04	0.04	0.05	0.05	0.04
Mg	0.1	287.7	275.9	272.3	293.0	304.1	285.9	286.1	289.2	279.9	292.9	281.8	271.6	201.7	197.6	220.4	253.7	201.9	256.6	196.7	242.1	223.0
Mn	0.006	ǂ	ǂ	ǂ	ǂ	0.009	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ
Mo	0.05	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ
Na	0.05	173.94	164.05	167.40	167.50	172.60	163.62	162.08	164.09	161.31	164.99	163.48	161.91	142.85	142.82	143.49	156.33	142.19	157.53	147.25	154.49	152.19
NH$_4^+$-N	§	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.03	0.01	0.00	0.01
NO$_3^-$-N	§	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	2.50	2.02	2.76	2.60	2.15	2.82
Ni	0.03	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ
P	0.1	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ
Pb	0.1	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ
S	0.1	697.9	685.7	671.6	758.1	812.5	685.6	733.0	699.0	669.9	763.4	673.5	617.0	440.1	429.5	505.0	598.7	469.5	602.7	440.1	582.9	507.4
Se	0.3	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ
Si	0.1	5.6	5.4	5.4	8.2	9.2	8.0	8.0	7.9	7.8	8.4	8.3	8.2	6.3	6.2	6.5	8.3	6.5	8.2	6.7	7.8	7.2
Sr	0.009	1.507	1.538	1.483	2.147	2.362	1.776	2.175	1.901	1.803	2.476	1.935	1.585	0.978	0.920	1.357	1.786	1.268	1.771	1.079	1.737	1.328
Ti	0.01	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ
V	0.03	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ
Zn	0.02	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ
pH(U)^x	§	7.4	7.5	7.5	7.5	7.5	7.4	7.4	7.5	7.5	7.6	7.6	7.5	7.5	7.6	7.6	7.5	7.5	7.5	7.5	7.6	7.6
pH(F)^w	§	8.8	8.7	8.8	8.7	8.8	8.7	8.9	8.6	8.9	8.5	8.6	8.6	8.4	8.6	8.4	8.2	8.2	7.8	7.9	8.3	8.2
EC^v(U)	§	3.1	3.2	3.1	3.1	3.1	3.2	3.2	3.1	3.2	3.3	3.2	3.2	3.5	3.6	3.5	3.5	3.5	3.5	3.5	3.5	3.5
EC(F)	§	3.5	3.4	3.4	3.5	3.5	3.5	3.5	3.3	3.4	3.5	3.5	3.5	3.5	3.2	3.4	3.6	3.1	3.2	3.2	3.2	3.2
IS^u(U)	§	0.040	0.041	0.040	0.041	0.041	0.041	0.042	0.041	0.041	0.043	0.042	0.042	0.045	0.046	0.046	0.045	0.046	0.045	0.046	0.045	0.046
IS(F)	§	0.046	0.045	0.044	0.045	0.046	0.046	0.046	0.043	0.045	0.046	0.045	0.046	0.046	0.041	0.044	0.046	0.040	0.042	0.042	0.042	0.042
IS$_{mod}^t$	§	0.061	0.060	0.058	0.065	0.069	0.060	0.063	0.061	0.058	0.065	0.059	0.054	0.040	0.040	0.046	0.053	0.043	0.054	0.041	0.052	0.046
ID^s	§	9.0	9.0	8.3	7.9	8.2	9.5	8.6	8.2	8.4	7.2	8.2	8.6	8.7	8.9	9.2	8.6	8.6	8.0	8.2	7.3	7.6

^{z} denotes detection limit; ^{y} denotes alkalinity in mg/L C; ^{x} samples left unfrozen prior to analysis; ^{w} samples frozen prior to analysis; ^{v} electrical conductivity in dS/m; ^{u} ionic strength calculated from EC in mol/L; ^{t} ionic strength calculated using GEOCHEM; ^{s} ion difference in percentage of free cationic charge relative to total cationic charge; ǂ denotes content below detection limit; § denotes data unavailable.

Table 4. Pore water chemical analyses from the time trial Gypsum treatment (mg/L).

Param.	DL[z]	Time of Sampling (days)						
		1	7	14	28	60	80	90
Al	0.2	2.8	2.9	2.4	2.3	1.6	2.0	1.7
As	0.03	╪	╪	╪	╪	╪	╪	╪
B	0.04	╪	0.04	╪	╪	╪	╪	╪
Ba	0.005	╪	0.009	╪	╪	╪	0.012	╪
Ca	0.05	651.20	633.20	607.30	552.30	383.00	472.60	447.30
Cd	0.01	╪	╪	╪	╪	╪	╪	╪
Co	0.01	╪	╪	╪	╪	╪	╪	╪
CO_3^--C[y]	§	§	§	§	6.18	6.49	6.79	6.79
Cr	0.02	╪	╪	╪	╪	╪	╪	╪
Cu	0.01	╪	╪	╪	╪	╪	╪	╪
Fe	0.01	╪	╪	╪	╪	╪	╪	╪
K	0.2	0.9	1.1	0.8	1.1	1.1	1.3	0.8
Li	0.04	╪	╪	╪	╪	╪	╪	╪
Mg	0.1	0.6	0.9	1.0	1.4	1.7	1.9	2.1
Mn	0.006	0.022	0.028	0.024	0.024	0.027	0.031	0.032
Mo	0.05	╪	╪	╪	╪	╪	╪	╪
Na	0.05	1.40	1.38	1.24	1.35	1.25	1.30	1.23
NH_4^+-N	§	0.00	0.00	0.00	0.00	0.00	0.00	0.00
NO_3^--N	§	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ni	0.03	╪	╪	╪	╪	╪	╪	╪
P	0.1	╪	╪	╪	╪	╪	╪	╪
Pb	0.1	╪	╪	╪	╪	╪	╪	╪
S	0.1	507.0	494.1	474.5	429.5	296.8	365.3	347.2
Se	0.3	╪	╪	╪	╪	╪	╪	╪
Si	0.1	0.1	0.2	0.2	0.3	0.5	0.6	0.6
Sr	0.009	1.889	2.551	3.020	2.916	2.257	2.648	2.525
Ti	0.01	0.04	0.04	0.02	0.02	0.01	0.02	╪
V	0.03	╪	╪	╪	╪	╪	╪	╪
Zn	0.02	0.04	╪	╪	╪	╪	╪	╪
pH(U)[x]	§	6.7	7.0	7.2	7.3	7.4	7.5	7.6
pH(F)[w]	§	§	§	§	7.6	7.7	7.6	7.6
EC[v](U)	§	1.9	2.0	2.0	1.9	1.9	2.0	2.1
EC(F)	§	§	§	2.0	2.1	1.9	2.0	1.8
IS[u](U)	§	0.025	0.026	0.026	0.025	0.025	0.027	0.027
IS(F)	§	§	§	0.026	0.027	0.024	0.026	0.023
ISmod[t]	§	0.044	0.043	0.041	0.038	0.028	0.033	0.032
ID[s]	§	4.3	3.9	3.5	4.2	4.4	4.9	4.1

[z] denotes detection limit; [y] denotes alkalinity in mg/L C; [x] samples left unfrozen prior to analysis; [w] samples frozen prior to analysis; [v] electrical conductivity in dS/m; [u] ionic strength calculated from EC in mol/L; [t] ionic strength calculated using GEOCHEM; [s] ion difference in percentage of free cationic charge relative to total cationic charge; ╪ denotes content below detection limit; § denotes data unavailable.

Table 5. Pore water chemical analyses from PG1:S0(60) (mg/L).

		Sample and Replicate Number																				
Param.	DL^z	1r1	1r2	1r3	2r1	2r2	2r3	3r1	3r2	3r3	4r1	4r2	4r3	5r1	5r2	5r3	6r1	6r2	6r3	7r1	7r2	7r3
Al	0.2	11.8	12.8	12.6	16.4	15.9	17.3	22.9	21.6	29.6	11.0	10.2	10.5	71.9	57.2	54.6	11.6	12.4	12.5	59.2	69.5	68.7
As	0.03	ǂ	ǂ	ǂ	0.55	0.54	0.59	0.86	0.77	0.92	ǂ	ǂ	ǂ	0.95	0.76	0.74	ǂ	ǂ	ǂ	0.45	0.52	0.50
B	0.04	ǂ	ǂ	ǂ	0.26	0.27	0.28	0.42	0.37	0.41	ǂ	ǂ	ǂ	0.30	0.25	0.25	ǂ	ǂ	ǂ	0.27	0.30	0.28
Ba	0.005	0.027	0.032	0.025	0.017	0.023	0.019	0.027	0.022	0.009	0.017	0.017	0.014	0.028	0.011	0.023	0.012	0.027	0.017	ǂ	0.007	ǂ
Ca	0.05	444.10	429.30	419.40	771.00	740.60	742.10	643.90	581.90	837.90	437.20	404.50	414.00	633.80	601.80	575.30	379.90	441.50	367.40	487.40	561.00	556.40
Cd	0.01	0.40	0.47	0.45	5.21	5.13	5.84	7.36	6.79	8.64	0.28	0.24	0.26	6.76	5.08	4.78	0.37	0.38	0.42	2.26	2.59	2.59
Co	0.01	ǂ	ǂ	ǂ	ǂ	0.01	ǂ	0.04	0.03	0.02	ǂ	ǂ	ǂ	0.02	ǂ	0.01	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ
CO_3^{2-}-C^y	§	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Cr	0.02	0.02	0.03	ǂ	0.44	0.46	0.50	0.55	0.52	0.63	0.06	0.04	0.03	0.48	0.34	0.33	0.06	0.08	0.08	0.05	0.08	0.06
Cu	0.01	0.68	0.79	0.74	9.84	8.86	9.78	16.5	15.6	19.7	0.82	0.65	0.64	12.9	9.38	8.62	1.30	1.26	1.32	1.21	1.50	1.46
Fe	0.01	0.03	0.03	0.03	0.88	0.90	0.97	1.04	0.97	1.17	0.12	0.09	0.09	0.73	0.55	0.53	0.09	0.11	0.12	0.06	0.10	0.08
K	0.2	2.9	3.4	3.2	200	200	210	290	260	280	5.6	5.4	5.3	170	160	140	3.7	3.9	3.5	150	160	160
Li	0.04	ǂ	ǂ	ǂ	0.20	0.21	0.22	0.38	0.34	0.37	ǂ	ǂ	ǂ	0.22	0.16	0.16	ǂ	ǂ	ǂ	ǂ	0.05	ǂ
Mg	0.1	0.6	0.7	1.0	17	16	19	36	33	44	0.5	0.5	0.8	33	25	23	0.6	0.7	0.9	24	27	28
Mn	0.006	0.046	0.051	0.057	1.646	1.622	1.847	3.910	3.615	4.635	0.039	0.033	0.038	1.538	1.167	1.088	0.054	0.055	0.063	0.568	0.653	0.658
Mo	0.05	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	0.10	0.06	0.07	ǂ	ǂ	ǂ	0.08	0.10	0.08
Na	0.05	4.45	4.89	4.73	219	212	231	322	291	347	7.70	7.38	7.57	185	164	150	5.61	5.70	5.48	85.4	91.5	92.5
NH_4^+-N	§	1.64	1.82	1.80	192	179	177	242	235	231	1.35	1.36	1.36	99.8	98.5	97.4	2.35	2.27	2.29	51.0	51.9	53.8
NO_3^--N	§	0.14	0.14	0.15	28.5	27.8	27.4	57.0	56.5	54.0	0.20	0.24	0.19	9.86	9.60	9.32	0.22	0.21	0.21	2.67	2.58	2.61
Ni	0.03	0.04	0.06	0.04	1.96	1.93	2.19	2.54	2.34	2.96	0.04	0.04	ǂ	2.86	2.14	2.03	ǂ	0.05	0.05	1.53	1.78	1.76
P	0.1	75.8	83.0	80.5	924	1120	1060	1240	1040	1100	74.4	67.9	69.7	764	698	847	83.1	85.3	86.8	443	425	496
Pb	0.1	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	0.2	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	0.1	ǂ
S	0.1	310.5	296.8	290.0	427.9	410.4	390.3	418.4	371.3	526.1	316.0	292.6	300.1	389.4	390.3	385.6	280.3	327.3	269.2	334.8	374.9	372.4
Se	0.3	0.6	0.6	0.6	0.6	0.6	0.7	1.1	1.0	1.1	0.4	0.4	0.4	2.3	1.8	1.8	0.8	0.9	0.9	6.9	7.6	7.5
Si	0.1	2.5	2.6	2.6	12	13	9.8	15	14	19	3.0	3.0	2.9	19	17	17	3.9	4.1	3.7	13	14	15
Sr	0.009	6.633	6.598	6.630	12.07	11.66	12.60	9.527	8.817	11.99	6.912	6.465	6.433	9.641	8.549	8.090	5.979	6.730	5.715	5.913	6.980	6.960
Ti	0.01	0.03	0.04	0.03	0.02	0.03	0.02	0.03	0.02	0.01	0.02	0.02	0.02	0.03	0.02	0.04	0.02	0.04	0.03	0.02	0.03	0.02
V	0.03	0.12	0.15	0.13	1.24	1.22	1.37	1.68	1.58	2.03	0.26	0.23	0.23	2.84	2.14	2.00	0.42	0.45	0.49	0.42	0.51	0.49
Zn	0.02	0.73	0.86	0.91	22.8	22.3	25.3	28.7	26.5	33.9	0.49	0.42	0.48	32.5	24.4	23.2	0.66	0.61	0.68	13.6	15.7	15.8
pH(U)^x	§	4.0	3.9	4.0	3.1	3.1	3.1	3.0	3.0	3.0	3.6	3.6	3.6	3.0	3.0	3.0	3.4	3.4	3.4	3.8	3.6	3.7
pH(F)^w	§	3.9	3.7	3.8	3.0	3.0	3.0	3.0	3.0	3.0	3.5	3.6	3.6	3.0	3.0	3.0	3.3	3.3	3.3	3.7	3.7	3.7
EC^v(U)	§	2.1	2.2	2.2	5.3	5.1	5.1	6.3	6.2	6.0	2.2	2.2	2.2	4.4	4.5	4.4	2.3	2.3	2.3	3.5	3.4	3.5
EC(F)	§	2.0	1.5	1.8	5.2	5.1	5.2	6.1	6.1	6.1	1.7	1.9	1.7	4.2	4.3	4.2	1.6	1.9	1.7	3.2	3.4	3.4
IS^u(U)	§	0.028	0.028	0.028	0.068	0.066	0.066	0.082	0.081	0.078	0.029	0.029	0.029	0.057	0.058	0.057	0.030	0.030	0.030	0.045	0.045	0.045
IS(F)	§	0.026	0.020	0.023	0.067	0.066	0.067	0.079	0.079	0.079	0.023	0.024	0.022	0.055	0.056	0.055	0.021	0.024	0.022	0.042	0.044	0.044
IS$_{mod}^t$	§	0.031	0.030	0.030	0.075	0.075	0.074	0.083	0.075	0.091	0.031	0.029	0.030	0.065	0.061	0.061	0.028	0.032	0.028	0.047	0.052	0.052
ID^s	§	13	13	14	27	15	22	18	24	26	11	12	12	32	28	15	8.9	9	9.3	24	31	26

^{z} denotes detection limit; ^{y} denotes alkalinity in mg/L C; ^{x} samples left unfrozen prior to analysis; ^{w} samples frozen prior to analysis; ^{v} electrical conductivity in dS/m; ^{u} ionic strength calculated from EC in mol/L; ^{t} ionic strength calculated using GEOCHEM; ^{s} ion difference in percentage of free cationic charge relative to total cationic charge; ǂ denotes content below detection limit; § denotes data unavailable.

Table 6. Pore water chemical analyses from PG1:S0(80) (mg/L).

		Sample and Replicate Number																				
Param.	DL^z	1r1	1r2	1r3	2r1	2r2	2r3	3r1	3r2	3r3	4r1	4r2	4r3	5r1	5r2	5r3	6r1	6r2	6r3	7r1	7r2	7r3
Al	0.2	12.7	14.5	13.9	20.3	19.6	18.3	28.6	28.8	26.8	13.0	12.9	13.9	72.6	72.0	75.2	13.1	15.0	14.7	67.9	64.4	70.8
As	0.03	‡	‡	‡	0.64	0.61	0.59	0.96	0.93	0.85	0.03	‡	0.04	0.93	0.92	0.92	‡	‡	‡	0.52	0.48	0.51
B	0.04	‡	‡	‡	0.30	0.29	0.27	0.43	0.42	0.40	‡	‡	‡	0.29	0.29	0.27	‡	‡	‡	0.29	0.27	0.29
Ba	0.005	0.030	0.031	0.022	0.030	0.032	0.02	0.016	0.033	0.031	0.024	0.022	0.026	0.028	0.026	0.024	0.021	0.018	0.010	‡	0.014	0.010
Ca	0.05	446.70	483.40	458.70	862.10	876.10	834.20	682.60	749.00	613.00	626.40	616.00	610.90	637.00	669.90	687.90	419.70	445.80	478.00	611.50	540.40	576.80
Cd	0.01	0.46	0.53	0.51	6.58	6.28	5.84	9.34	8.93	7.81	0.31	0.30	0.32	6.67	6.49	6.76	0.42	0.49	0.49	2.75	2.45	2.71
Co	0.01	‡	‡	‡	0.02	0.02	0.01	0.04	0.05	0.04	‡	‡	‡	0.02	0.02	0.01	‡	‡	‡	‡	‡	‡
CO_3^{2-}-C^y	§	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Cr	0.02	0.02	0.03	‡	0.49	0.50	0.43	0.59	0.60	0.49	0.06	0.05	0.08	0.42	0.42	0.44	0.07	0.08	0.06	0.06	0.06	0.07
Cu	0.01	0.76	0.87	0.80	11.9	10.4	9.40	20.4	19.80	16.8	0.84	0.72	0.99	12.2	11.5	11.7	1.30	1.46	1.36	1.45	1.36	1.51
Fe	0.01	0.02	0.03	0.02	1.10	1.07	0.95	1.29	1.29	1.02	0.08	0.07	0.36	0.72	0.70	0.77	0.09	0.10	0.09	0.04	0.08	0.08
K	0.2	3.3	3.5	3.3	200	200	200	290	280	260	5.6	5.7	5.9	160	160	160	4.2	4.4	4.2	140	140	150
Li	0.04	‡	‡	‡	0.25	0.24	0.22	0.40	0.40	0.37	‡	‡	‡	0.19	0.20	0.18	‡	‡	‡	0.04	0.04	0.05
Mg	0.1	0.9	0.8	1.2	22	20	19	45	44	40	0.6	0.6	1.0	32	32	32	0.7	0.8	1.0	30	26	30
Mn	0.006	0.058	0.061	0.070	2.090	1.997	1.854	5.047	4.812	4.173	0.044	0.043	0.052	1.522	1.492	1.557	0.066	0.076	0.078	0.711	0.627	0.696
Mo	0.05	‡	‡	‡	‡	‡	‡	‡	‡	‡	‡	‡	‡	0.12	0.11	0.11	‡	‡	‡	0.10	0.08	0.12
Na	0.05	4.90	5.46	5.47	233	225	224	354	330	308	8.23	8.02	8.42	173	175	174	6.45	6.85	6.46	88.2	84.8	89.3
NH_4^+-N	§	1.67	1.82	1.84	179	177	176	239	235	227	1.48	1.43	1.26	99.5	98.3	95.8	2.39	2.33	2.33	48.7	47.7	50.8
NO_3^--N	§	0.15	0.15	0.15	28.2	27.4	27.5	57.5	56	54	0.2	0.19	0.2	9.64	9.54	9.26	0.25	0.24	0.25	2.52	2.44	2.54
Ni	0.03	0.07	0.06	0.05	2.51	2.40	2.20	3.22	3.13	2.72	0.05	0.04	0.05	2.84	2.80	2.91	0.05	0.06	0.04	1.90	1.69	1.88
P	0.1	85.9	98.5	95.9	989	920	1340	1050	1020	976	87.4	84.6	88.3	860	683	856	99.1	112	108	468	376	410
Pb	0.1	‡	‡	‡	‡	‡	‡	‡	‡	‡	‡	‡	‡	0.1	0.1	‡	‡	‡	‡	‡	0.1	‡
S	0.1	307.6	334.6	319.6	437.1	452.4	442.9	396.2	440.7	366.3	459.9	450.9	458.8	395.0	421.8	426.1	304.9	320.8	346.7	404.6	358.8	378.9
Se	0.3	0.7	0.7	0.6	0.8	0.7	0.6	1.2	1.2	1.1	0.5	0.5	0.8	2.2	2.2	2.1	1.0	1.1	1.0	7.6	7.0	7.6
Si	0.1	2.8	3.0	3.1	12	13	14	12	15	12	4.3	4.3	5.1	19	20	23	4.3	4.9	4.4	15	15	16
Sr	0.009	6.959	7.871	7.511	14.29	14.19	13.53	11.27	11.42	9.907	9.511	9.293	9.536	9.821	10.11	10.51	7.272	8.008	7.943	7.028	6.655	7.197
Ti	0.01	0.04	0.04	0.02	0.04	0.04	0.03	0.01	0.03	0.03	0.04	0.03	0.04	0.04	0.04	0.03	0.03	0.03	0.02	0.03	0.03	0.03
V	0.03	0.14	0.16	0.14	1.58	1.50	1.36	2.16	2.10	1.82	0.26	0.23	0.46	2.75	2.72	2.84	0.41	0.48	0.46	0.50	0.45	0.53
Zn	0.02	0.84	0.98	1.04	28.8	27.4	25.4	36.7	35.1	30.4	0.48	0.45	0.49	32.4	31.6	33.0	0.71	0.79	0.79	16.9	15.0	16.6
pH(U)^x	§	4.0	3.9	4.0	3.0	3.0	3.0	3.0	3.0	3.0	3.6	3.6	3.7	3.0	3.0	3.0	3.4	3.4	3.4	3.6	3.6	3.6
pH(F)^w	§	3.8	3.8	3.8	3.0	3.0	3.0	3.0	3.0	3.0	3.6	3.7	3.2	3.0	3.0	3.0	3.5	3.4	3.4	3.7	3.6	3.7
EC^v(U)	§	2.2	2.2	2.2	5.2	5.2	5.2	6.1	6.1	6.1	2.3	2.3	2.3	4.6	4.6	4.5	2.3	2.3	2.3	3.4	3.4	3.4
EC(F)	§	1.4	1.5	1.5	5.3	5.1	4.8	6.0	6.1	5.6	2.2	2.2	1.9	4.0	4.0	4.3	1.4	1.7	1.5	3.3	3.0	3.2
IS^u(U)	§	0.029	0.029	0.029	0.067	0.069	0.067	0.079	0.08	0.079	0.029	0.029	0.029	0.059	0.060	0.059	0.030	0.030	0.030	0.044	0.044	0.045
IS(F)	§	0.018	0.020	0.019	0.068	0.066	0.062	0.078	0.079	0.073	0.028	0.028	0.025	0.053	0.053	0.056	0.019	0.022	0.019	0.042	0.039	0.042
ISmod^t	§	0.032	0.034	0.033	0.08	0.079	0.082	0.083	0.085	0.076	0.043	0.042	0.042	0.066	0.066	0.069	0.031	0.033	0.035	0.055	0.049	0.052
ID^s	§	13	12	11	31	32	11	34	33	32	10	11	7.4	26	36	27	9.3	9.7	9.1	28	34	34

^{z} denotes detection limit; ^{y} denotes alkalinity in mg/L C; ^{x} samples left unfrozen prior to analysis; ^{w} samples frozen prior to analysis; ^{v} electrical conductivity in dS/m; ^{u} ionic strength calculated from EC in mol/L; ^{t} ionic strength calculated using GEOCHEM; ^{s} ion difference in percentage of free cationic charge relative to total cationic charge; ‡ denotes content below detection limit; § denotes data unavailable.

Table 7. Pore water chemical analyses from PG1:S0(U80) (mg/L).

Param.	DL^z	Sample and Replicate Number																				
		1r1	1r2	1r3	2r1	2r2	2r3	3r1	3r2	3r3	4r1	4r2	4r3	5r1	5r2	5r3	6r1	6r2	6r3	7r1	7r2	7r3
Al	0.2	15.7	16.8	16.6	22.4	21.8	20.9	32.3	31.9	33.2	12.5	13.0	13.6	79.5	79.2	79.6	17.5	18.0	18.7	75.9	73.6	74.0
As	0.03	╪	╪	╪	0.66	0.64	0.61	1.03	0.99	0.95	╪	╪	╪	0.96	0.95	0.97	╪	╪	╪	0.54	0.51	0.52
B	0.04	╪	╪	╪	0.29	0.28	0.27	0.46	0.43	0.42	╪	╪	╪	0.29	0.28	0.29	╪	╪	╪	0.30	0.26	0.27
Ba	0.005	0.034	0.037	0.031	0.025	0.026	0.029	0.036	0.032	0.035	0.023	0.015	0.021	0.034	0.029	0.03	0.028	0.022	0.021	0.018	0.009	0.017
Ca	0.05	712.50	712.50	726.30	1086.3	1081.3	1026.8	1013.4	992.40	986.70	604.60	635.30	617.80	838.70	856.20	870.50	686.70	698.70	732.70	795.00	777.90	758.40
Cd	0.01	0.52	0.57	0.55	7.06	6.92	6.58	10.2	9.81	9.46	0.30	0.30	0.31	7.17	7.08	7.12	0.55	0.56	0.59	2.84	2.73	2.76
Co	0.01	╪	╪	╪	0.02	0.01	0.02	0.06	0.05	0.05	╪	╪	╪	0.02	0.02	0.02	╪	╪	╪	╪	╪	╪
CO_3^{2-}-C^y	§	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Cr	0.02	0.03	0.04	0.02	0.55	0.56	0.52	0.70	0.69	0.64	0.06	0.04	0.07	0.48	0.48	0.49	0.10	0.10	0.09	0.08	0.07	0.08
Cu	0.01	0.86	0.94	0.88	12.8	11.6	10.7	22.4	22.0	20.6	0.81	0.72	0.96	13.2	12.6	12.4	1.73	1.70	1.67	1.51	1.54	1.55
Fe	0.01	0.03	0.04	0.02	1.26	1.23	1.18	1.56	1.50	1.37	0.09	0.08	0.37	0.86	0.86	0.85	0.13	0.13	0.12	0.11	0.11	0.12
K	0.2	3.4	3.8	3.6	210	200	190	290	290	280	5.7	5.3	5.7	160	160	160	4.3	4.5	4.3	150	140	150
Li	0.04	╪	╪	╪	0.24	0.24	0.23	0.44	0.42	0.40	╪	╪	╪	0.20	0.20	0.19	╪	╪	╪	0.05	╪	0.05
Mg	0.1	1.0	0.8	1.3	23	22	21	50	48	48	0.5	0.5	0.9	34	34	34	1.0	1.0	1.3	31	29	31
Mn	0.006	0.065	0.068	0.077	2.246	2.213	2.104	5.507	5.304	5.096	0.042	0.042	0.049	1.642	1.634	1.64	0.086	0.087	0.096	0.735	0.704	0.713
Mo	0.05	╪	╪	╪	╪	╪	╪	╪	╪	╪	╪	╪	╪	0.10	0.10	0.09	╪	╪	╪	0.10	0.11	0.10
Na	0.05	5.45	5.88	5.80	239	236	222	356	346	332	7.82	8.00	8.24	177	178	178	7.18	7.25	7.37	89.5	87.1	87.6
NH_4^+-N	§	1.67	1.82	1.84	179	177	176	239	235	227	1.48	1.43	1.26	99.5	98.3	95.8	2.39	2.33	2.33	48.7	47.7	50.8
NO_3^--N	§	0.15	0.15	0.15	28.2	27.4	27.5	57.5	56.0	54.0	0.20	0.19	0.20	9.64	9.54	9.26	0.25	0.24	0.25	2.52	2.44	2.54
Ni	0.03	0.07	0.08	0.06	2.68	2.63	2.50	3.55	3.44	3.31	0.04	╪	0.04	3.06	3.05	3.07	0.07	0.06	0.06	1.96	1.88	1.91
P	0.1	102	108	106	1480	1460	1440	1690	1660	1590	83.8	85.9	87.1	1110	1070	1080	122	125	128	630	632	649
Pb	0.1	╪	╪	╪	╪	╪	╪	╪	╪	╪	╪	╪	╪	0.1	╪	0.1	╪	╪	╪	0.1	╪	╪
S	0.1	514.8	506.7	521.0	582.7	580.7	549.8	618.3	603.8	603.6	440.6	463.8	462.8	535.2	549.8	562.6	507.9	512.3	537.4	532.7	521.4	508.0
Se	0.3	0.8	0.8	0.7	0.8	0.7	0.7	1.4	1.3	1.2	0.5	0.4	0.7	2.3	2.3	2.3	1.2	1.2	1.2	7.9	7.5	7.7
Si	0.1	19.2	19.3	19.8	31.5	30.9	28.9	32.6	31.6	31.0	14.8	15.4	15.2	33.5	34.1	34.9	25.5	26.1	26.9	40.1	38.8	38.5
Sr	0.009	9.462	9.754	9.767	16.00	15.85	15.03	13.36	13.20	12.99	9.203	9.609	9.542	11.20	11.35	11.51	9.937	10.19	10.63	8.530	8.277	8.249
Ti	0.01	0.05	0.05	0.04	0.04	0.04	0.04	0.05	0.04	0.04	0.04	0.03	0.04	0.05	0.04	0.05	0.05	0.04	0.04	0.04	0.03	0.04
V	0.03	0.15	0.17	0.15	1.71	1.67	1.59	2.40	2.33	2.27	0.24	0.20	0.45	2.99	2.99	2.99	0.53	0.54	0.57	0.55	0.56	0.55
Zn	0.02	0.95	1.06	1.12	31.0	30.4	28.7	40.1	38.8	37.2	0.46	0.46	0.48	34.9	34.7	34.8	0.94	0.91	0.95	17.4	16.9	17.1
pH	§	4.0	3.9	4.0	3.0	3.0	3.0	3.0	3.0	3.0	3.6	3.6	3.7	3.0	3.0	3.0	3.4	3.4	3.4	3.6	3.6	3.6
EC^x	§	2.2	2.2	2.2	5.2	5.2	5.2	6.1	6.1	6.1	2.3	2.3	2.3	4.6	4.6	4.5	2.3	2.3	2.3	3.4	3.5	3.5
IS^w	§	0.029	0.029	0.029	0.067	0.068	0.067	0.079	0.080	0.079	0.030	0.029	0.029	0.059	0.060	0.059	0.030	0.030	0.030	0.044	0.045	0.045
ISmod^v	§	0.048	0.048	0.048	0.097	0.096	0.092	0.011	0.011	0.01	0.042	0.043	0.043	0.081	0.081	0.082	0.047	0.048	0.050	0.067	0.066	0.066
ID^u	§	9.8	12	11	11	12	10	12	11	12	11	11	7.9	15	17	16	8.5	9.4	9.6	17	16	16

^{z} denotes detection limit; ^{y} denotes alkalinity in mg/L C; ^{x} electrical conductivity in dS/m; ^{w} ionic strength calculated from EC in mol/L; ^{v} ionic strength calculated using GEOCHEM; ^{u} ion difference in percentage of free cationic charge relative to total cationic charge; ╪ denotes content below detection limit; § denotes data unavailable.

Table 8. Pore water chemical analyses from PG10:S1(60) (mg/L).

		Sample and Replicate Number																				
Param.	DL^z	1r1	1r2	1r3	2r1	2r2	2r3	3r1	3r2	3r3	4r1	4r2	4r3	5r1	5r2	5r3	6r1	6r2	6r3	7r1	7r2	7r3
Al	0.2	1.7	1.7	1.3	5.4	5.1	5.2	5.3	5.0	5.3	1.6	2.2	1.9	6.1	5.2	5.1	1.8	1.8	1.8	7.5	9.4	10
As	0.03	ǂ	ǂ	ǂ	0.41	0.36	0.37	0.55	0.53	0.53	ǂ	ǂ	ǂ	0.56	0.66	0.68	ǂ	ǂ	ǂ	0.35	0.47	0.52
B	0.04	ǂ	ǂ	ǂ	0.15	0.14	0.15	0.22	0.22	0.21	ǂ	ǂ	ǂ	0.16	0.18	0.19	ǂ	ǂ	ǂ	0.17	0.21	0.24
Ba	0.005	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	0.007	0.017	ǂ	ǂ	ǂ	ǂ	0.016	0.012	0.005	ǂ	ǂ	ǂ
Ca	0.05	374.60	394.10	433.40	592.80	527.40	550.80	594.40	552.40	579.80	329.20	398.20	401.00	446.70	433.00	428.40	355.50	375.40	398.70	464.80	473.20	447.70
Cd	0.01	0.02	0.02	0.01	1.80	1.56	1.54	2.40	2.29	2.32	ǂ	0.01	ǂ	1.77	2.23	2.25	0.02	0.02	0.02	0.82	1.21	1.30
Co	0.01	ǂ	ǂ	ǂ	0.01	0.01	0.02	0.03	0.03	0.03	ǂ	ǂ	ǂ	0.02	0.02	0.02	ǂ	ǂ	ǂ	ǂ	0.02	0.02
CO_3^{2-}-C^y	§	2.78	2.53	2.47	4.12	3.71	2.66	0.62	1.54	0.00	1.98	2.47	2.16	0.00	0.00	0.00	1.85	2.16	2.16	0.00	0.93	1.85
Cr	0.02	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	0.03	0.03	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ
Cu	0.01	ǂ	ǂ	ǂ	0.82	0.66	0.94	1.89	1.52	1.44	ǂ	ǂ	ǂ	0.83	1.34	1.31	ǂ	ǂ	ǂ	0.06	0.10	0.12
Fe	0.01	ǂ	ǂ	ǂ	ǂ	0.03	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ
K	0.2	4.6	4.4	4.0	140	130	130	180	180	180	6.4	6.4	5.8	100	120	120	4.8	4.8	4.8	120	130	140
Li	0.04	ǂ	ǂ	ǂ	0.23	0.22	0.22	0.30	0.29	0.29	ǂ	ǂ	ǂ	0.20	0.22	0.22	ǂ	ǂ	ǂ	0.09	0.12	0.15
Mg	0.1	82.7	89.9	103	95.5	89.9	85.9	79.0	81.8	83.8	91.0	94.6	92.6	86.0	92.0	89.8	72.8	81.8	82.9	71.5	107	112
Mn	0.006	0.222	0.249	0.338	2.882	2.651	2.561	3.643	3.599	3.637	0.301	0.394	0.440	2.311	2.485	2.383	0.157	0.187	0.200	1.625	2.611	2.596
Mo	0.05	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ
Na	0.05	34.07	36.13	39.88	191.4	174.5	177.5	228.8	229.9	230.5	37.12	38.16	38.22	144.6	158.5	160.1	28.34	31.20	32.40	95.37	111.0	120.5
NH_4^+-N	§	0.04	0.07	0.14	145	140	145	176	173	169	0.03	0.02	0.10	77.5	92.2	89.7	0.09	0.07	0.05	36.5	36.1	38.0
NO_3^--N	§	0.95	0.90	0.36	20.6	19.7	21.6	42.8	42.6	41.7	0.04	0.04	0.03	2.43	8.16	6.81	0.11	0.03	0.03	0.48	0.03	0.34
Ni	0.03	ǂ	ǂ	ǂ	1.37	1.21	1.18	1.48	1.44	1.43	ǂ	ǂ	ǂ	1.36	1.72	1.76	ǂ	ǂ	ǂ	0.86	1.31	1.38
P	0.1	2.3	2.5	3.3	760	820	860	770	800	660	2.7	2.7	2.7	530	530	640	5.6	5.9	5.9	340	430	470
Pb	0.1	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ
Se	0.1	0.4	0.4	0.4	0.9	0.9	0.9	1.2	1.2	1.3	0.7	0.7	0.6	1.9	1.7	1.7	1.0	1.1	1.2	5.9	7.4	8.0
S	0.3	416.5	441.3	499.2	444.8	403.9	413.8	469.0	449.7	474.9	388.9	447.6	447.6	393.3	360.1	353.6	380.8	409.0	432.2	427.5	444.9	429.2
Si	0.1	5.2	8.8	8.4	9.7	10	11	15	11	15	4.3	6.2	7.7	8.5	7.7	10	6.0	4.7	4.8	7.3	6.7	9.2
Sr	0.009	2.561	2.722	3.009	4.991	4.497	4.628	4.364	4.053	4.204	2.021	2.392	2.425	2.532	2.486	2.438	2.305	2.459	2.612	2.789	2.967	2.864
Ti	0.01	0.02	0.02	ǂ	0.02	0.02	0.02	0.03	0.03	0.02	0.01	0.03	ǂ	0.02	0.02	0.02	0.03	0.02	0.01	0.02	0.02	0.02
V	0.03	0.03	0.04	ǂ	0.07	0.06	0.07	0.09	0.08	0.08	ǂ	0.03	ǂ	0.19	0.26	0.30	0.07	0.07	0.06	0.08	0.07	0.13
Zn	0.02	ǂ	ǂ	ǂ	7.48	6.52	6.74	9.24	8.56	8.77	ǂ	ǂ	ǂ	8.65	10.8	10.7	ǂ	ǂ	ǂ	4.67	6.89	7.40
pH(U)^x	§	6.3	6.4	6.3	4.4	4.4	4.4	4.3	4.4	4.4	6.1	6.1	6.2	4.4	4.4	4.4	6.0	6.0	6.0	4.5	4.5	4.5
pH(F)^w	§	5.3	5.2	5.2	4.2	4.2	4.2	4.0	4.0	4.0	4.6	5.0	4.9	3.9	3.9	3.8	4.6	4.8	4.9	4.0	4.1	4.2
EC^v(U)	§	2.4	2.4	2.5	4.7	4.7	4.7	5.1	5.1	5.8	2.5	2.5	2.5	3.6	3.9	3.9	2.4	2.6	2.4	3.4	3.4	3.4
EC(F)	§	2.2	2.4	2.3	4.7	4.7	4.7	5.2	5.2	5.0	2.3	2.4	2.4	3.8	3.8	4.1	1.8	2.1	2.0	2.8	2.7	3.1
IS^u(U)	§	0.032	0.032	0.032	0.061	0.061	0.061	0.066	0.066	0.076	0.033	0.032	0.032	0.047	0.050	0.050	0.031	0.034	0.032	0.044	0.044	0.044
IS(F)	§	0.029	0.032	0.030	0.061	0.061	0.061	0.067	0.067	0.065	0.029	0.031	0.031	0.049	0.054	0.057	0.023	0.027	0.025	0.036	0.035	0.040
ISmod^t	§	0.037	0.039	0.044	0.069	0.067	0.067	0.073	0.071	0.071	0.036	0.040	0.040	0.054	0.054	0.055	0.035	0.037	0.039	0.049	0.054	0.054
ID^s	§	5.2	5.4	3.4	14	7.1	4.1	13	10	18	7.7	7.4	7.1	8.2	17	7.5	6.8	6.9	5.9	6.6	6.7	6.2

^{z} denotes detection limit; ^{y} denotes alkalinity in mg/L C; ^{x} samples left unfrozen prior to analysis; ^{w} samples frozen prior to analysis; ^{v} electrical conductivity in dS/m; ^{u} ionic strength calculated from EC in mol/L; ^{t} ionic strength calculated using GEOCHEM; ^{s} ion difference in percentage of free cationic charge relative to total cationic charge; ǂ denotes content below detection limit; § denotes data unavailable.

Table 9. Pore water chemical analyses from PG10:S1(80) (mg/L).

		Sample and Replicate Number																				
Param.	DL^z	1r1	1r2	1r3	2r1	2r2	2r3	3r1	3r2	3r3	4r1	4r2	4r3	5r1	5r2	5r3	6r1	6r2	6r3	7r1	7r2	7r3
Al	0.2	1.8	1.4	1.1	ǂ	6.5	5.7	5.5	4.7	5.1	1.7	1.8	1.8	7.6	5.6	6.1	1.8	1.7	1.7	9.7	8.0	10
As	0.03	ǂ	ǂ	ǂ	0.46	0.44	0.41	0.50	0.43	0.48	ǂ	ǂ	ǂ	0.61	0.58	0.62	ǂ	ǂ	ǂ	0.40	0.33	0.44
B	0.04	ǂ	ǂ	ǂ	0.18	0.16	0.17	0.19	0.17	0.17	ǂ	ǂ	ǂ	0.18	0.16	0.17	ǂ	ǂ	ǂ	0.19	0.17	0.21
Ba	0.005	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	0.008	0.013	0.010	ǂ	ǂ	ǂ	ǂ	0.007	ǂ	ǂ	ǂ
Ca	0.05	410.90	334.50	403.10	456.50	546.80	410.90	518.00	487.00	446.80	363.80	362.10	344.60	391.90	382.40	463.20	407.70	395.30	378.50	448.40	393.60	518.00
Cd	0.01	0.02	0.02	ǂ	2.06	1.93	1.79	2.20	1.78	2.35	ǂ	ǂ	0.01	2.12	1.82	2.05	0.02	0.02	0.02	1.09	0.83	1.17
Co	0.01	ǂ	ǂ	ǂ	0.03	0.02	0.03	0.02	0.01	ǂ	ǂ	ǂ	ǂ	0.05	0.02	0.03	ǂ	ǂ	ǂ	0.01	0.01	0.02
CO_3^{2-}-C^y	§	2.59	2.47	2.16	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.85	1.85	0.00	0.00	0.00	1.85	2.16	1.85	0.00	0.18	0.00
Cr	0.02	ǂ	ǂ	ǂ	0.03	0.03	0.02	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	0.03	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ
Cu	0.01	ǂ	ǂ	ǂ	0.98	0.84	1.12	1.70	1.17	1.45	ǂ	ǂ	ǂ	1.01	1.10	1.21	ǂ	ǂ	ǂ	0.08	0.06	0.09
Fe	0.01	ǂ	ǂ	ǂ	ǂ	0.01	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	0.02	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ
K	0.2	4.5	4.8	3.5	140	140	140	180	160	190	6.2	6.4	5.8	100	110	110	4.9	4.8	4.9	120	110	130
Li	0.04	ǂ	ǂ	ǂ	0.29	0.27	0.26	0.27	0.24	0.27	ǂ	ǂ	ǂ	0.25	0.20	0.22	ǂ	ǂ	ǂ	0.11	0.10	0.13
Mg	0.1	73.0	86.0	85.8	114	115	103	75.2	65.2	88.4	91.2	92.1	67.1	104	76.0	82.4	87.0	83.6	82.6	96.8	73.4	103
Mn	0.006	0.207	0.252	0.293	3.507	3.465	3.161	3.522	2.939	3.917	0.289	0.385	0.317	3.007	2.192	2.34	0.181	0.188	0.192	2.705	2.023	2.871
Mo	0.05	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ
Na	0.05	32.44	35.50	35.10	200.6	197.5	187.0	223.3	197.6	241.9	37.24	37.31	31.24	144.2	146.0	145.9	32.48	31.60	29.92	102.3	90.36	108.8
NH_4^+-N	§	0.05	0.06	0.07	142	138	142	169	167	161	0.04	0.02	0.08	74.1	87.6	90.7	0.09	0.11	0.04	32.3	31.7	33.8
NO_3^--N	§	1.13	1.12	0.48	18.8	18.2	19.0	39.4	39.2	37.8	0.04	0.02	0.03	0.01	3.22	4.86	0.03	0.03	0.04	0.00	0.01	0.01
Ni	0.03	ǂ	ǂ	ǂ	1.59	1.51	1.38	1.34	1.09	1.42	ǂ	ǂ	ǂ	1.62	1.37	1.56	ǂ	ǂ	ǂ	1.14	0.85	1.22
P	0.1	2.1	2.1	2.7	660	600	470	530	530	790	2.4	2.6	2.1	550	550	560	5.6	5.5	5.4	380	310	400
Pb	0.1	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ
S	0.1	431.9	390.5	440.5	357.3	430.1	329.4	440.4	414.0	391.5	416.9	418.4	371.3	362.6	336.8	387.8	445.5	429.5	417.0	435.6	382.5	495.0
Se	0.3	0.4	0.4	ǂ	1.6	1.5	1.5	1.4	1.2	1.4	0.6	0.8	0.6	2.5	1.9	2.0	1.2	1.1	1.2	7.6	6.7	8.2
Si	0.1	5.2	5.8	7.3	5.5	6.5	4.9	8.7	7.5	5.0	4.4	4.0	5.6	8.5	9.0	3.9	4.6	6.0	4.9	6.7	5.8	9.4
Sr	0.009	2.850	2.404	2.883	4.249	4.684	3.774	3.701	3.388	3.412	2.271	2.260	2.111	2.297	2.186	2.573	2.694	2.627	2.502	2.763	2.464	3.225
Ti	0.01	0.02	ǂ	ǂ	0.02	0.02	0.02	0.01	0.01	ǂ	0.02	0.02	0.02	0.03	0.02	0.03	0.01	0.01	0.02	ǂ	0.01	0.02
V	0.03	0.03	ǂ	ǂ	0.10	0.08	0.09	0.06	0.05	0.04	ǂ	ǂ	ǂ	0.20	0.19	0.22	0.06	0.06	0.07	0.04	ǂ	0.03
Zn	0.02	ǂ	ǂ	ǂ	8.52	7.96	7.66	8.36	6.60	8.87	ǂ	ǂ	ǂ	10.1	8.73	9.74	ǂ	ǂ	ǂ	6.06	4.55	6.50
pH(U)^x	§	6.4	6.4	6.3	4.3	4.3	4.3	4.2	4.3	4.3	6.1	6.1	6.1	4.3	4.3	4.3	6.0	6.0	6.0	4.4	4.4	4.4
pH(F)^w	§	5.2	5.2	5.1	4.0	3.9	3.9	3.9	3.9	4.0	2.2	4.7	4.9	3.8	4.0	3.8	5.0	5.0	5.0	4.0	4.0	4.0
EC^v(U)	§	2.6	2.6	2.6	4.7	4.7	4.7	5.0	5.1	5.0	2.6	2.6	2.5	4.0	4.2	4.2	2.5	2.4	2.5	3.4	3.4	3.4
EC(F)	§	1.9	2.1	2.0	4.9	4.7	4.0	4.0	3.7	5.0	1.9	2.0	1.8	3.1	3.5	3.1	1.7	1.8	1.6	2.4	2:3	2.7
IS^u(U)	§	0.033	0.033	0.033	0.061	0.061	0.061	0.064	0.066	0.066	0.033	0.033	0.033	0.053	0.054	0.055	0.032	0.032	0.032	0.044	0.044	0.044
IS(F)	§	0.025	0.027	0.026	0.064	0.061	0.053	0.053	0.048	0.065	0.024	0.026	0.023	0.040	0.046	0.04	0.022	0.024	0.021	0.031	0.029	0.035
IS$_{mod}$^{t}	§	0.039	0.035	0.039	0.061	0.066	0.055	0.065	0.061	0.066	0.038	0.038	0.034	0.052	0.050	0.055	0.04	0.039	0.037	0.051	0.045	0.057
ID^s	§	5.2	4.9	6.0	22	25	33	24	21	9.7	7.3	6.7	6.0	8.8	8.2	10	5.5	6.1	5.2	6.1	6.1	5.4

^{z} denotes detection limit; ^{y} denotes alkalinity in mg/L C; ^{x} samples left unfrozen prior to analysis; ^{w} samples frozen prior to analysis; ^{v} electrical conductivity in dS/m; ^{u} ionic strength calculated from EC in mol/L; ^{t} ionic strength calculated using GEOCHEM; ^{s} ion difference in percentage of free cationic charge relative to total cationic charge; ǂ denotes content below detection limit; § denotes data unavailable.

Table 10. Pore water chemical analyses from PG1:S1(60) (mg/L).

Param.	DL^z	Sample and Replicate Number																				
		1r1	1r2	1r3	2r1	2r2	2r3	3r1	3r2	3r3	4r1	4r2	4r3	5r1	5r2	5r3	6r1	6r2	6r3	7r1	7r2	7r3
Al	0.2	1.0	0.9	1.0	1.5	1.3	1.4	1.7	1.6	1.6	0.7	0.9	0.7	1.9	1.8	1.7	0.7	0.7	0.6	2.4	2.6	2.3
As	0.03	ǂ	ǂ	ǂ	0.26	0.27	0.25	0.34	0.48	0.47	ǂ	ǂ	ǂ	0.32	0.26	0.31	ǂ	ǂ	ǂ	0.24	0.28	0.22
B	0.04	ǂ	0.05	0.04	0.20	0.20	0.20	0.24	0.27	0.27	0.06	0.06	0.06	0.17	0.15	0.17	ǂ	ǂ	0.04	0.19	0.21	0.18
Ba	0.005	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	0.007	0.008	0.012	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ
Ca	0.05	309.70	285.90	320.70	338.50	364.80	289.70	384.40	368.80	384.70	165.95	225.10	140.55	272.90	289.20	195.67	201.40	215.50	179.57	287.60	332.60	287.30
Cd	0.01	ǂ	ǂ	ǂ	0.13	0.12	0.14	0.20	0.29	0.26	ǂ	ǂ	ǂ	0.16	0.13	0.17	ǂ	ǂ	ǂ	0.08	0.10	0.07
Co	0.01	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ
CO_3^{2-}-C^y	§	8.34	10.5	10.5	8.96	10.8	8.34	0.00	14.2	13.3	9.88	9.57	8.65	4.01	4.32	3.71	7.41	7.72	8.65	4.01	4.01	4.32
Cr	0.02	ǂ	ǂ	ǂ	ǂ	ǂ	0.02	0.02	0.03	0.03	ǂ	ǂ	ǂ	ǂ	ǂ	0.02	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ
Cu	0.01	ǂ	ǂ	ǂ	0.01	0.02	0.02	0.04	0.09	0.08	ǂ	ǂ	ǂ	0.02	0.01	0.02	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ
Fe	0.01	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	0.01	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ
K	0.2	10	10	10	74	75	73	87	120	130	11	11	9.2	55	52	56	8.6	9.2	9.4	55	57	52
Li	0.04	ǂ	ǂ	ǂ	0.32	0.32	0.31	0.37	0.46	0.46	0.06	0.06	0.06	0.28	0.24	0.27	ǂ	ǂ	ǂ	0.20	0.23	0.20
Mg	0.1	180.5	278.8	293.8	324.5	342.4	315.9	361.4	326.9	309.6	196.7	237.7	153.5	226.4	178.7	220.3	179.5	241.9	227.6	280.4	355.1	269.0
Mn	0.006	ǂ	ǂ	ǂ	3.027	2.818	3.110	3.759	4.326	3.982	ǂ	ǂ	ǂ	1.919	1.704	1.950	ǂ	ǂ	ǂ	3.308	4.009	2.910
Mo	0.05	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ
Na	0.05	134.68	166.89	169.95	256.20	263.20	244.80	286.40	329.90	333.00	143.59	157.36	121.76	194.44	174.53	190.52	123.85	143.29	139.39	172.03	200.40	172.70
NH_4^+-N	§	0.00	0.08	0.07	62.8	62.4	65.3	69.3	110	110	0.07	0.11	0.01	34.0	32.3	33.8	0.01	0.01	0.01	11.3	11.8	11.9
NO_3^--N	§	2.01	2.09	1.90	14.7	13.5	15.4	24.0	23.2	33.1	1.08	0.36	0.19	0.02	0.02	0.02	0.83	0.16	0.30	0.04	0.04	0.00
Ni	0.03	ǂ	ǂ	ǂ	0.29	0.28	0.32	0.37	0.66	0.59	ǂ	ǂ	ǂ	0.36	0.30	0.38	ǂ	ǂ	ǂ	0.23	0.26	0.18
P	0.1	0.1	ǂ	ǂ	240	230	240	230	380	380	ǂ	ǂ	ǂ	220	190	220	ǂ	ǂ	ǂ	140	160	120
Pb	0.1	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ
S	0.1	541.2	674.8	726.4	795.2	842.2	733.6	895.0	817.6	813.6	459.4	566.3	375.3	560.7	515.2	485.9	457.9	560.4	510.0	652.9	793.3	647.1
Se	0.3	ǂ	ǂ	ǂ	0.8	0.6	0.8	1.0	1.0	0.9	ǂ	ǂ	ǂ	1.6	1.3	1.6	ǂ	ǂ	ǂ	4.7	5.4	4.5
Si	0.1	5.1	7.9	7.8	19	26	18	26	24	28	4.3	4.9	3.3	17	7.4	5.4	5.2	6.5	5.2	8.4	11	10
Sr	0.009	2.040	1.978	2.188	2.170	2.237	1.891	2.107	2.106	2.149	1.031	1.378	0.846	1.241	1.252	0.874	1.363	1.486	1.225	1.505	1.718	1.457
Ti	0.01	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	0.01	ǂ	0.01	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ
V	0.03	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ
Zn	0.02	ǂ	ǂ	ǂ	0.23	0.18	0.25	0.27	0.44	0.39	ǂ	ǂ	ǂ	0.36	0.30	0.40	ǂ	ǂ	ǂ	0.21	0.24	0.17
pH(U)^x	§	7.5	7.6	7.4	5.4	5.5	5.3	5.3	5.3	5.3	7.5	7.5	7.5	5.1	5.1	5.1	7.6	7.6	7.6	5.2	5.2	5.2
pH(F)^w	§	8.0	7.8	8.2	5.2	5.4	5.2	3.5	5.4	5.3	7.9	7.8	8.2	7.6	4.7	4.6	7.6	8.2	8.0	4.7	4.8	4.8
EC^v(U)	§	3.6	3.6	3.4	4.7	4.6	4.6	4.7	4.9	5.2	3.6	3.6	3.5	4.4	4.5	4.3	3.4	3.5	3.4	4.0	4.0	4.0
EC(F)	§	2.8	3.0	3.1	4.1	4.0	4.0	4.8	5.1	5.1	3.1	3.3	3.3	4.3	4.1	4.2	3.1	3.1	3.1	4.0	3.8	3.8
IS^u(U)	§	0.046	0.046	0.044	0.061	0.060	0.060	0.061	0.064	0.067	0.046	0.046	0.046	0.057	0.059	0.056	0.045	0.045	0.045	0.052	0.052	0.052
IS(F)	§	0.037	0.039	0.041	0.053	0.052	0.052	0.062	0.066	0.067	0.040	0.043	0.043	0.056	0.053	0.055	0.040	0.040	0.040	0.052	0.049	0.050
ISmod^t	§	0.048	0.059	0.063	0.077	0.080	0.073	0.085	0.086	0.085	0.042	0.050	0.035	0.057	0.052	0.052	0.042	0.05	0.046	0.061	0.073	0.061
ID^s	§	8.7	7.0	6.4	5.5	6.0	6.5	6.8	9.6	8.5	8.7	8.3	7.9	7.0	6.8	8.0	6.7	6.9	7.2	5.2	5.3	5.3

^{z} denotes detection limit; ^{y} denotes alkalinity in mg/L C; ^{x} samples left unfrozen prior to analysis; ^{w} samples frozen prior to analysis; ^{v} electrical conductivity in dS/m; ^{u} ionic strength calculated from EC in mol/L; ^{t} ionic strength calculated using GEOCHEM; ^{s} ion difference in percentage of free cationic charge relative to total cationic charge; ǂ denotes content below detection limit; § denotes data unavailable.

Table 11. Pore water chemical analyses from PG1:S1(80) (mg/L).

		Sample and Replicate Number																				
Param.	DL^z	1r1	1r2	1r3	2r1	2r2	2r3	3r1	3r2	3r3	4r1	4r2	4r3	5r1	5r2	5r3	6r1	6r2	6r3	7r1	7r2	7r3
Al	0.2	0.9	0.7	0.6	1.1	1.1	1.3	1.0	1.0	1.1	1.0	1.4	0.7	1.6	1.7	1.5	0.7	0.7	0.9	2.9	3.1	3.5
As	0.03	‡	‡	‡	0.26	0.22	0.21	0.33	0.40	0.23	‡	‡	‡	0.40	0.32	0.33	‡	‡	0.13	0.25	0.27	0.28
B	0.04	‡	0.04	0.05	0.19	0.18	0.18	0.21	0.23	0.20	0.07	0.06	0.05	0.17	0.15	0.15	0.04	‡	0.04	0.21	0.22	0.23
Ba	0.005	‡	‡	‡	‡	‡	‡	‡	‡	‡	0.008	0.009	‡	‡	‡	‡	‡	‡	0.100	‡	‡	‡
Ca	0.05	292.30	228.90	179.97	275.00	262.30	272.40	217.90	229.30	171.36	229.80	343.20	179.76	256.80	300.80	248.20	212.70	199.67	215.60	264.70	275.40	360.20
Cd	0.01	‡	‡	‡	0.13	0.10	0.12	0.17	0.23	0.14	‡	‡	‡	0.19	0.15	0.15	‡	‡	[illegible]	0.10	0.10	0.11
Co	0.01	‡	‡	‡	‡	‡	‡	‡	‡	‡	‡	‡	‡	‡	‡	‡	‡	‡	‡	‡	‡	‡
CO_3^{2-}-C^y	§	9.26	8.65	8.46	8.03	7.41	7.41	10.2	9.26	6.79	8.34	10.5	6.79	4.01	3.40	4.01	5.87	7.41	7.41	3.40	3.71	4.32
Cr	0.02	‡	‡	‡	‡	‡	‡	0.02	0.02	0.02	0.02	‡	‡	‡	‡	‡	‡	‡	0.14	‡	‡	‡
Cu	0.01	‡	‡	‡	0.01	0.02	0.02	0.05	0.07	0.02	‡	‡	‡	0.01	‡	‡	‡	‡	0.10	‡	‡	‡
Fe	0.01	‡	‡	‡	‡	‡	‡	‡	‡	0.01	‡	‡	‡	‡	‡	‡	‡	‡	0.12	‡	‡	‡
K	0.2	10	9.7	9.7	72	68	68	100	110	75	11	11	9.3	61	57	57	9.3	9.1	9.4	57	58	58
Li	0.04	‡	‡	‡	0.33	0.28	0.29	0.35	0.40	0.30	0.06	0.06	0.04	0.34	0.29	0.28	‡	‡	‡	0.24	0.27	0.28
Mg	0.1	255.2	230.8	208.8	346.9	275.7	258.4	210.0	279.0	238.7	223.6	284.6	178.4	303.9	227.2	223.1	216.4	218.0	213.9	306.9	349.6	388.6
Mn	0.006	‡	‡	‡	3.307	2.486	2.632	2.855	3.888	2.672	‡	‡	‡	2.522	2.127	1.935	‡	‡	0.119	4.027	4.322	4.552
Mo	0.05	‡	‡	‡	‡	‡	‡	‡	‡	‡	‡	‡	‡	‡	‡	‡	‡	‡	‡	‡	‡	‡
Na	0.05	160.03	144.81	140.77	251.10	224.50	216.60	255.70	292.60	227.80	151.32	165.37	129.13	221.40	193.35	188.50	139.59	137.46	135.20	178.71	195.48	204.40
NH_4^+-N	§	0.04	0.03	0.02	62.4	63.0	64.9	109	108	67.8	0.01	0.00	0.07	34.2	32.3	33.6	0.00	0.02	0.01	11.8	11.1	10.8
NO_3^--N	§	2.46	2.29	2.41	14.4	14.1	15.1	31.2	32.7	23.2	0.52	0.34	0.38	0.01	0.01	0.01	1.00	0.31	0.77	0.00	0.00	0.00
Ni	0.03	‡	‡	‡	0.32	0.25	0.28	0.41	0.56	0.27	‡	‡	‡	0.46	0.36	0.36	‡	‡	0.09	0.28	0.30	0.31
P	0.1	‡	‡	‡	228.9	185.7	197.2	258.1	313.8	160.0	‡	‡	‡	261.4	216.4	215.8	‡	‡	‡	145.2	151.6	158.0
Pb	0.1	‡	‡	‡	‡	‡	‡	‡	‡	‡	‡	‡	‡	‡	‡	‡	‡	‡	‡	‡	‡	‡
S	0.1	649.4	558.2	487.9	765.2	669.6	647.6	551.8	650.1	554.8	549.0	724.6	442.5	649.3	591.7	540.6	523.7	515.1	519.0	675.4	739.8	859.7
Se	0.3	‡	‡	‡	1.0	0.6	0.9	0.7	0.9	1.0	‡	‡	‡	1.9	1.7	1.6	‡	‡	‡	6.1	6.4	6.7
Si	0.1	7.2	6.3	5.6	15	14	17	7.3	7.3	6.0	4.1	5.1	3.6	7.3	12	11	5.6	6.0	6.0	8.1	8.9	14
Sr	0.009	2.012	1.601	1.282	1.688	1.587	1.669	1.204	1.279	0.942	1.462	2.096	1.112	1.134	1.251	1.033	1.480	1.404	1.489	1.449	1.494	1.882
Ti	0.01	‡	‡	‡	‡	‡	‡	‡	‡	‡	‡	‡	‡	‡	‡	‡	‡	‡	‡	‡	‡	‡
V	0.03	‡	‡	‡	‡	‡	‡	‡	‡	‡	‡	‡	‡	‡	‡	‡	‡	‡	‡	‡	‡	‡
Zn	0.02	‡	‡	‡	0.21	0.16	0.20	0.24	0.33	0.18	‡	‡	‡	0.41	0.33	0.33	‡	‡	0.14	0.26	0.26	0.58
pH(U)^x	§	7.5	7.5	7.5	5.3	5.3	5.2	5.3	5.4	5.4	7.6	7.6	7.6	5.2	5.1	5.2	7.6	7.6	7.6	5.1	5.1	5.1
pH(F)^w	§	7.7	8.0	7.8	5.4	5.4	5.4	5.5	5.6	5.2	7.8	7.8	7.6	5.0	4.8	4.9	7.3	7.5	7.8	4.7	4.8	4.8
EC^v(U)	§	3.6	3.5	3.6	4.7	4.6	4.6	5.2	5.2	4.8	3.5	3.5	3.5	4.5	4.4	4.4	3.4	3.4	3.5	4.1	4.1	4.1
EC(F)	§	2.7	2.5	2.6	3.7	3.6	3.5	4.0	4.3	3.9	2.7	3.4	2.6	3.9	3.6	3.5	2.7	2.7	2.8	3.4	3.2	3.6
IS^u(U)	§	0.047	0.046	0.046	0.061	0.059	0.060	0.068	0.068	0.062	0.046	0.045	0.045	0.058	0.057	0.057	0.044	0.044	0.045	0.054	0.053	0.053
IS(F)	§	0.035	0.032	0.034	0.048	0.047	0.046	0.052	0.056	0.051	0.035	0.045	0.034	0.050	0.047	0.045	0.035	0.035	0.036	0.045	0.042	0.047
ISmod^t	§	0.057	0.050	0.044	0.075	0.066	0.064	0.061	0.071	0.057	0.049	0.063	0.040	0.066	0.059	0.056	0.047	0.046	0.046	0.063	0.069	0.078
ID^s	§	6.0	6.4	7.0	7.0	7.3	7.2	11	9.4	9.3	7.9	7.5	7.3	6.4	5.8	8.5	6.9	6.7	7.1	5.0	6.0	5.9

^{z} denotes detection limit; ^{y} denotes alkalinity in mg/L C; ^{x} samples left unfrozen prior to analysis; ^{w} samples frozen prior to analysis; ^{v} electrical conductivity in dS/m; ^{u} ionic strength calculated from EC in mol/L; ^{t} ionic strength calculated using GEOCHEM; ^{s} ion difference in percentage of free cationic charge relative to total cationic charge; ‡ denotes content below detection limit; § denotes data unavailable.

Table 12. Pore water chemical analyses from PG0:S1(60) and PG0:S1(80) (mg/L).

		Time of Sampling (days) and Replicate Number					
Param.	DL[z]	60r1	60r2	60r3	80r1	80r2	80r3
Al	0.2	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ
As	0.03	0.08	0.07	0.07	0.07	0.08	0.08
B	0.04	0.05	ǂ	ǂ	ǂ	0.05	0.05
Ba	0.005	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ
Ca	0.05	108.18	107.90	109.68	121.56	114.27	113.10
Cd	0.01	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ
Co	0.01	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ
CO_3^{2-}-C[y]	§	28.41	28.25	25.32	28.41	26.25	25.63
Cr	0.02	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ
Cu	0.01	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ
Fe	0.01	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ
K	0.2	13.1	13.2	13.3	13.1	13.3	13.6
Li	0.04	0.07	0.07	0.06	0.07	0.08	0.07
Mg	0.1	292.1	282.4	303.3	332.1	320.5	324.8
Mn	0.006	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ
Mo	0.05	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ
Na	0.05	284.90	284.20	293.20	289.50	285.70	288.70
NH_4^+-N	§	5.10	5.12	5.42	5.50	5.09	5.26
NO_3^--N	§	5.10	5.12	5.42	5.50	5.09	5.26
Ni	0.03	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ
P	0.1	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ
Pb	0.1	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ
S	0.1	587.1	578.2	610.4	651.9	626.4	632.0
Se	0.3	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ
Si	0.1	3.1	3.0	3.0	3.1	2.9	2.9
Sr	0.009	1.111	1.101	1.139	1.255	1.181	1.177
Ti	0.01	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ
V	0.03	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ
Zn	0.02	ǂ	ǂ	ǂ	ǂ	ǂ	ǂ
pH(U)[x]	§	8.0	8.0	8.0	8.2	8.2	8.2
pH(F)[w]	§	9.0	8.9	8.9	9.0	8.8	8.9
EC[v](U)	§	3.2	3.2	3.2	3.1	3.0	3.0
EC(F)	§	3.1	3.1	3.1	3.1	3.2	3.1
IS[u](U)	§	0.041	0.041	0.041	0.04	0.04	0.039
IS(F)	§	0.041	0.04	0.040	0.041	0.041	0.041
ISmod[t]	§	0.054	0.054	0.056	0.059	0.058	0.058
ID[s]	§	15	15	15	14	14	14

[z] denotes detection limit; [y] denotes alkalinity in mg/L C; [x] samples left unfrozen prior to analysis; [w] samples frozen prior to analysis; [v] electrical conductivity in dS/m; [u] ionic strength calculated from EC in mol/L; [t] ionic strength calculated using GEOCHEM; [s] ion difference in percentage of free cationic charge relative to total cationic charge; ǂ denotes content below detection limit; § denotes data unavailable.